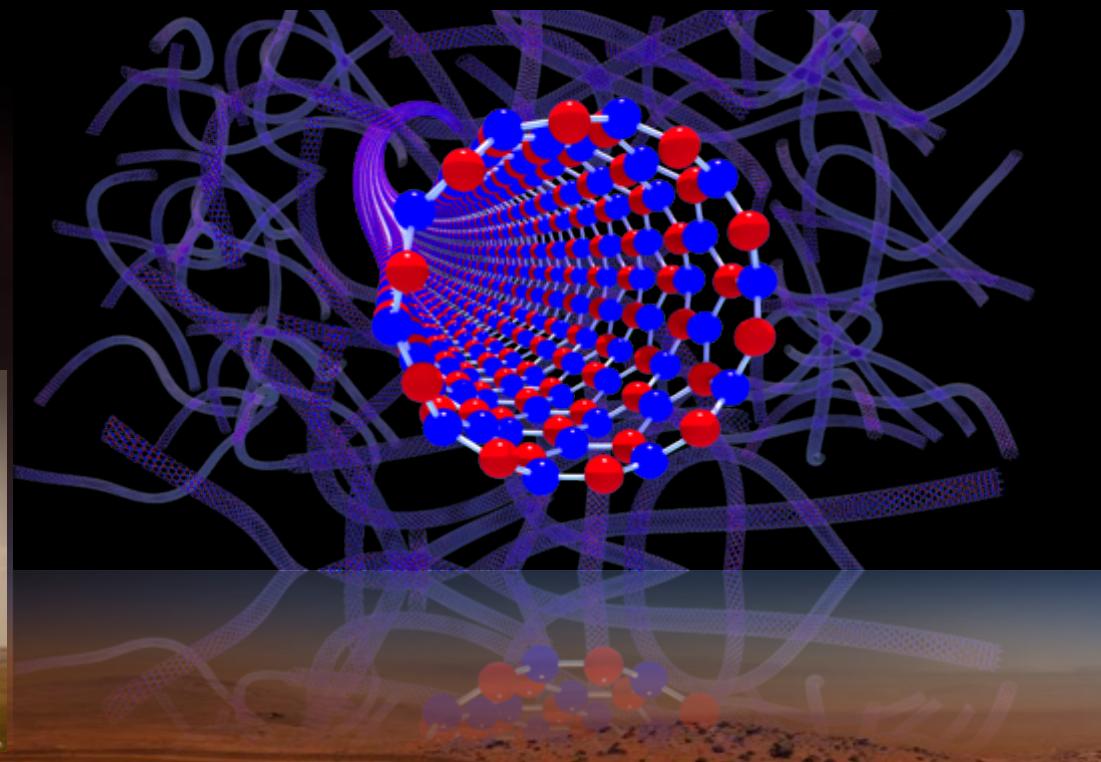
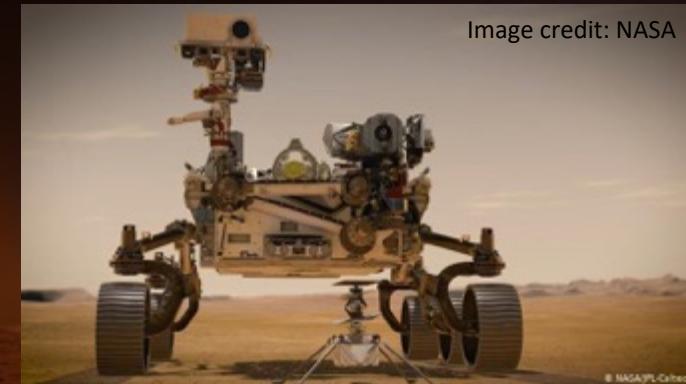




NASA Langley Research Center

Multifunctional Lightweight Structural Composites for Extreme Space Environments

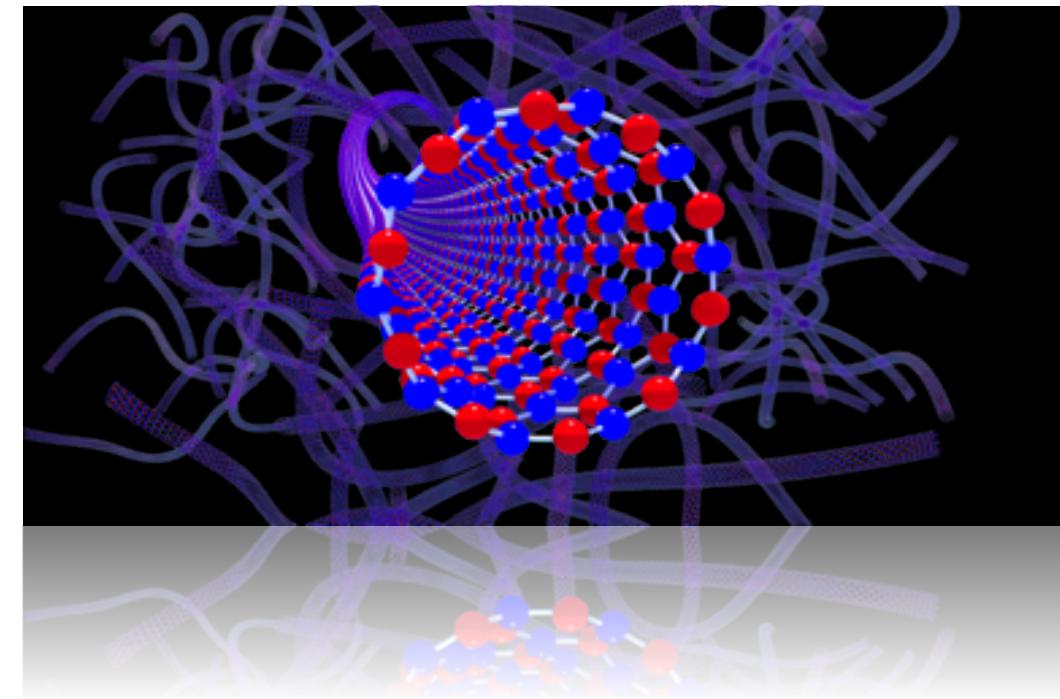
Cheol Park, Sang-Hyon Chu*, and Catharine Fay



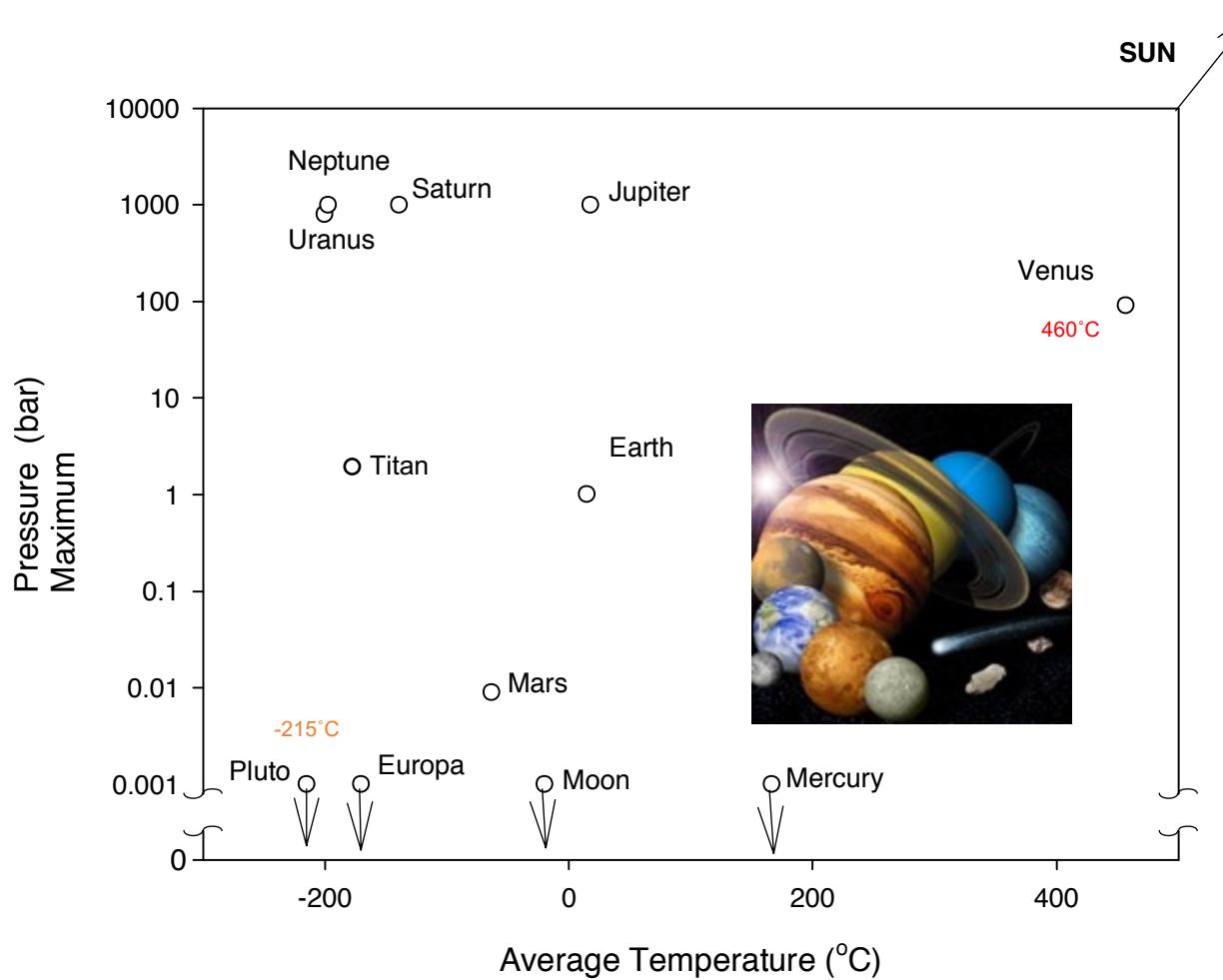
Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton VA USA

Outline

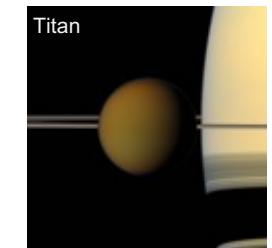
- Motivation: Extreme Environments in Space
- Current NASA Space Projects: Artemis Program
- Introduction of Boron Nitride Nanotube (BNNT)
- BNNT and BNNT Composite Application
- Multifunctional Properties in Extreme Environments
 - Dispersion and Purification
 - Mechanical Properties
 - Thermal Properties
 - Sensor/Actuator/Energy Harvester
 - Radiation Shielding
- Summary



Extreme Environments in Space Exploration



http://www.jpl.nasa.gov/solar_system/
17NASA Extreme Environments Tech Space missions Report FINAL



Hypersonic heat flux at atmospheric entry: Heat fluxes often exceeding 1 kW/cm²

Hypervelocity impact: Higher than 20 km/sec

Extreme temperatures: Lower than -240°C and Exceeding +460°C

Thermal cycling: Cycling between temperature extremes outside of the military standard range of -55°C to +125°C

High pressures: Exceeding 20 bars

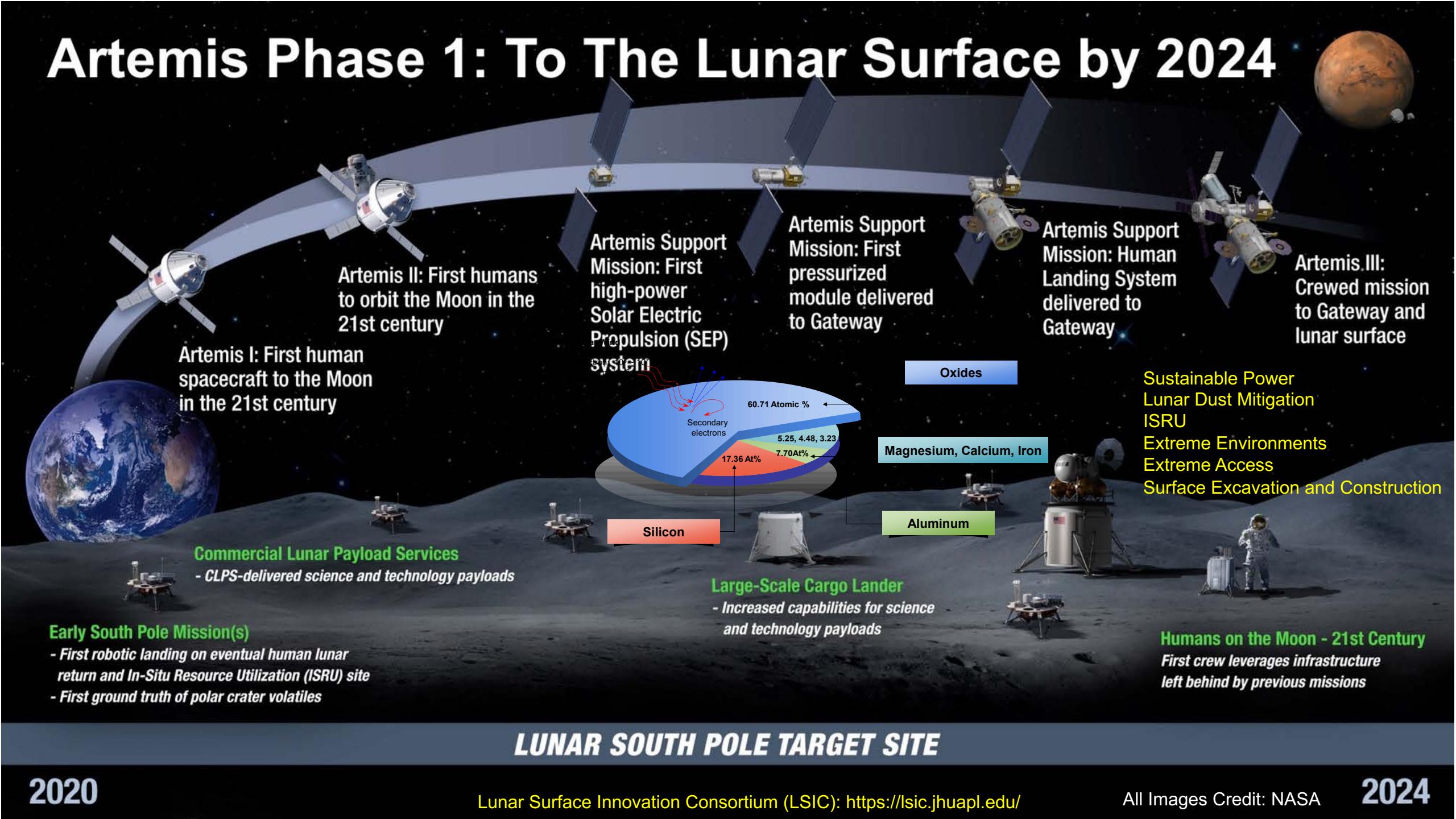
High radiation: Total ionizing dose (TID) exceeding 300 krad (Si), GCR, SPE, Neutron

Low and High gravity: microgravity on comets, 2.5g on Jupiter, launch, entry, descent

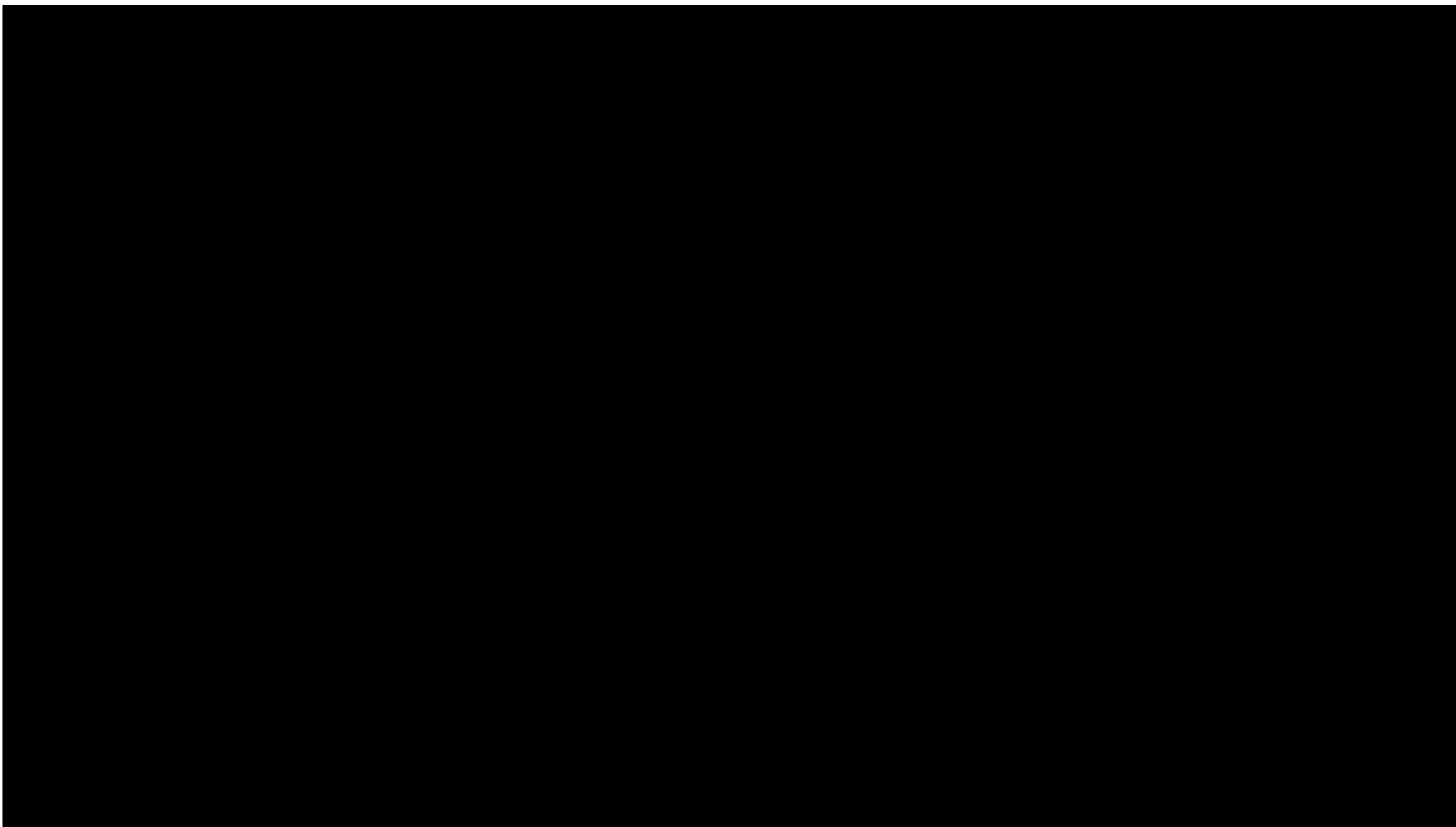
Artemis Program: Send 1st woman & next man to the Moon by 2024 (about \$40B), and then Mars and Beyond

All Images Credit: NASA

Artemis Phase 1: To The Lunar Surface by 2024



ISRU Landing Pad: Multipurpose Cassegrain System



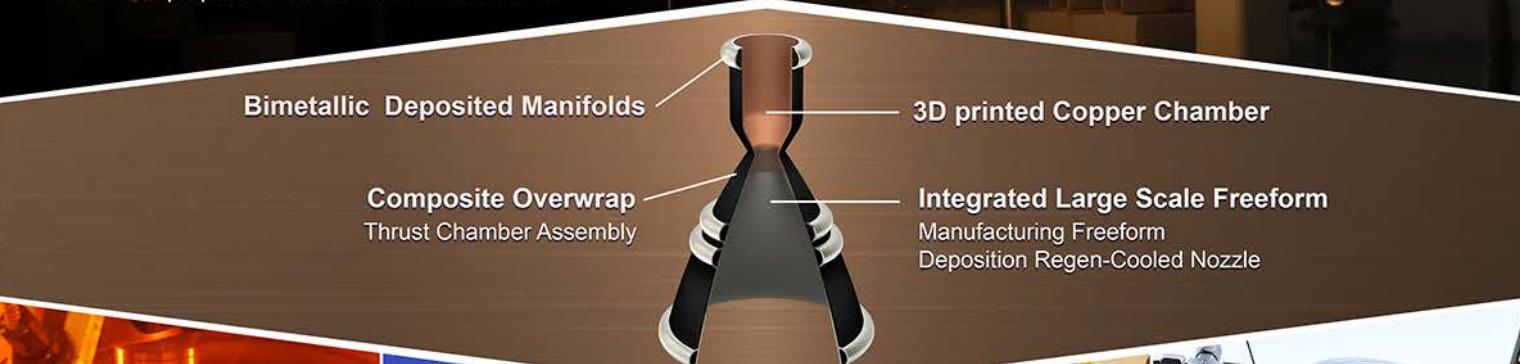
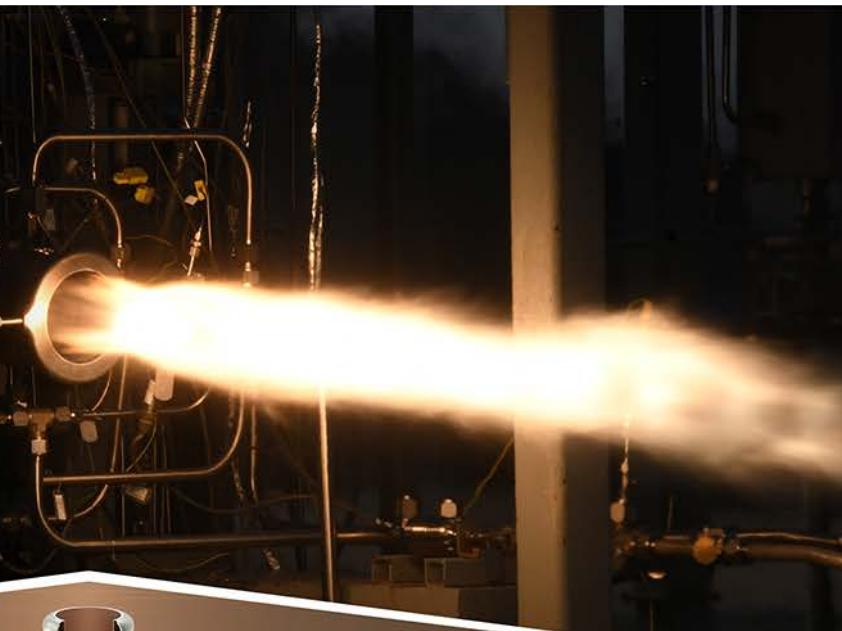
<https://www.youtube.com/watch?v=mpXdY2v5FDI&feature=youtu.be>

Rapid Analysis and Manufacturing Propulsion Technology (RAMPT)

Project Description: The RAMPT project is maturing novel design and manufacturing technologies to increase scale, significantly reduce cost, and improve performance for regeneratively-cooled thrust chamber assemblies, specifically the combustion chamber and nozzle for government and industry programs.

The high level RAMPT goals are to:

- 1) Develop additive and advanced manufacturing methods and design processes that enable new regeneratively-cooled thrust chamber assembly technology.
- 2) Identify and optimize additive manufacturing design and fabrication processes that reduce production lead times and analysis life cycle and
- 3) Engage academic, government and industry investments through public-private partnerships to facilitate infusion of technology and provide process development data and technology improvements across the propulsion and commercial industries.



PUBLIC AND PRIVATE PARTNERSHIPS



Large-Scale 3D Printing for Rocket Engines

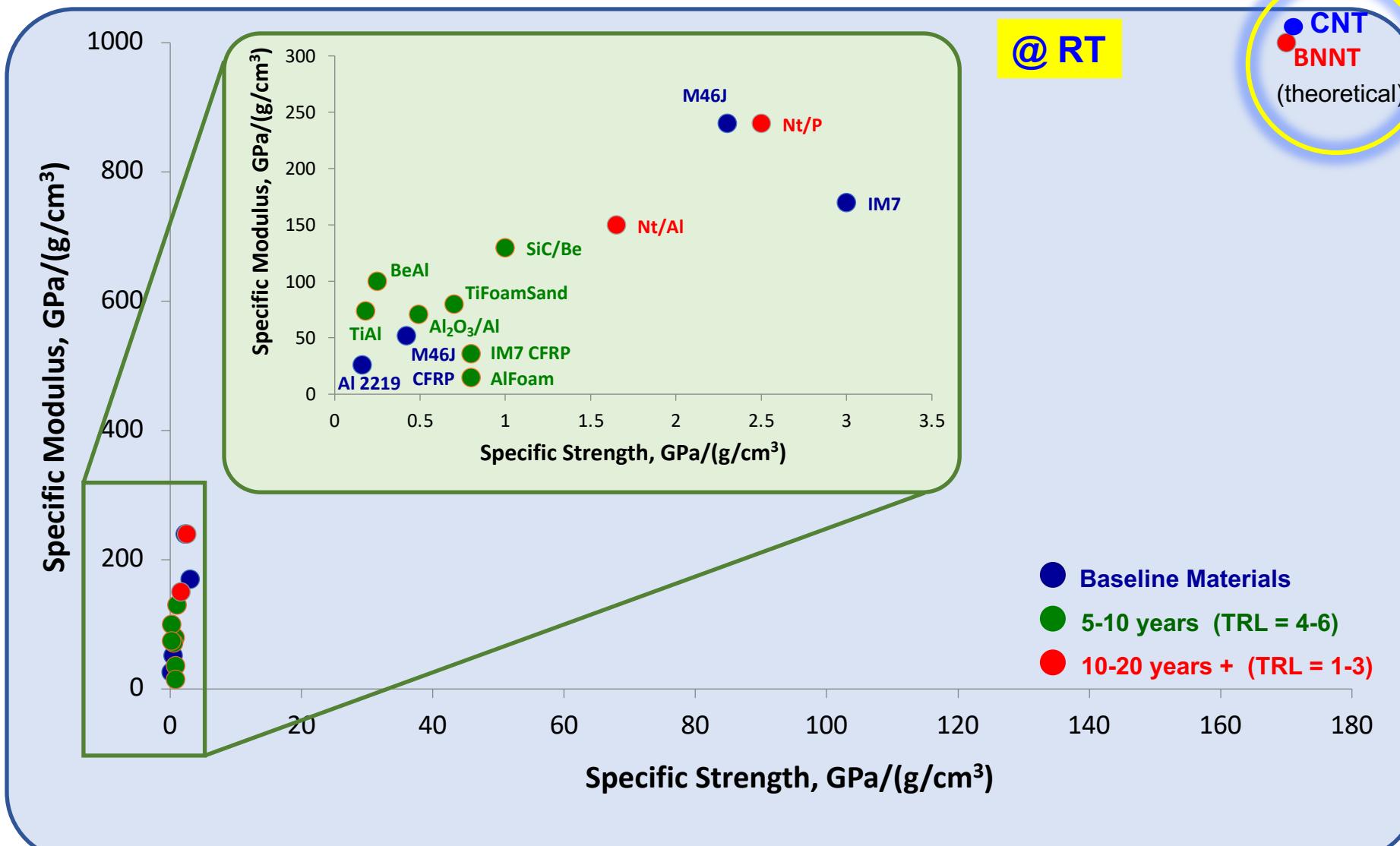
<https://www.youtube.com/watch?v=JHqdVU9Ebo&t=3s>



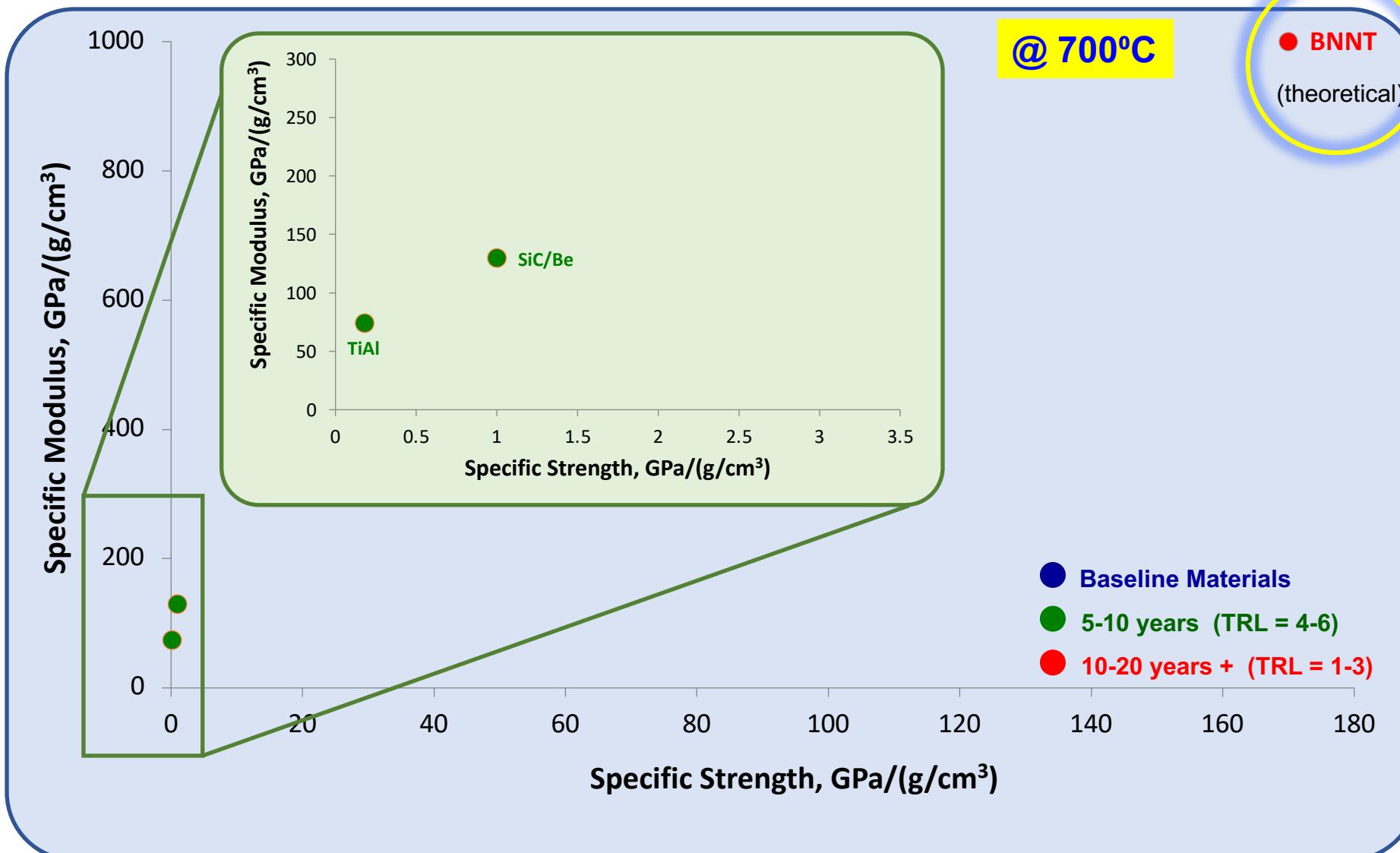
CAMX, Dallas, TX (2021)

All Images Video Credit: NASA

Motivation: Properties of Materials for Vehicle Structure



Motivation: Properties of Materials for Vehicle Structure

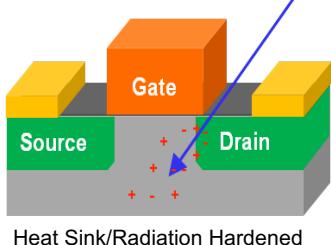


Nanotube Comparison (Theoretical)

	Carbon Nanotubes	Boron Nitride Nanotubes
Electric Properties	Metallic or semiconducting	Wide band gap (about 6.0 eV) Insulation, corrosion resistant
Mechanical Properties (Young's Modulus)	1.33 TPa (very stiff)	1.18 TPa (very stiff)
Thermal Conductivity	>3000 W/mK (highly conductive)	~300–3000 W/mK (highly conductive)
Thermal Oxidation Resistance	Stable up to 300-400 °C in air	Stable to over 900 °C in air
Neutron Absorption Cross-Section	C = 0.0035 barn	B = 767 barn (B ¹⁰ ~3800 barn) N = 1.9 barn Excellent radiation shielding
Polarity	No dipole	Permanent dipole Piezoelectric (0.25-0.4 C/m ²)
Surface Morphology	Smooth	Corrugated Better interfacial strength for composites, ionic bonding
Color	Black	White (can be colored)
Coefficient of Thermal Expansion	-1 x10 ⁻⁶ K ⁻¹ (very low)	-1 x 10 ⁻⁶ K ⁻¹ (very low)

Significance of the BNNT Innovation

- **Structural/Mechanical:** lightweight composite armor, thermal protection, engine components, and radiation shielding materials for **extreme environments**.
- **High stiffness as well as high toughness** for spacecraft and space suits, ultrastrong tethers, meteorite impact protection layers, protective gear for astronauts.
- **Space lubricants** without moisture.
- **High temperature** thermal protection systems (**TPS**) used in the **nose cap**, **wing leading edges**, **engine parts**, lubricants, and planetary **Entry, Descent, & Landing (EDL)** TPS.
- **Fire resistant and retardant**.
- **High temperature sensor, actuator, energy harvesting devices** in extreme environments.
- **Radiation shielding, UV (ultraviolet) protection**, and electromagnetic transparency while decreasing aircraft weight.
- **Radar transparency** mitigates Electromagnetic Interference (EMI) and Radio Frequency (RF) blackout.
- **Efficient zero-energy water filter and desalination membrane in microgravity**.



UV Protection
Cosmetic

Cancer
Diagnostic
Treatment

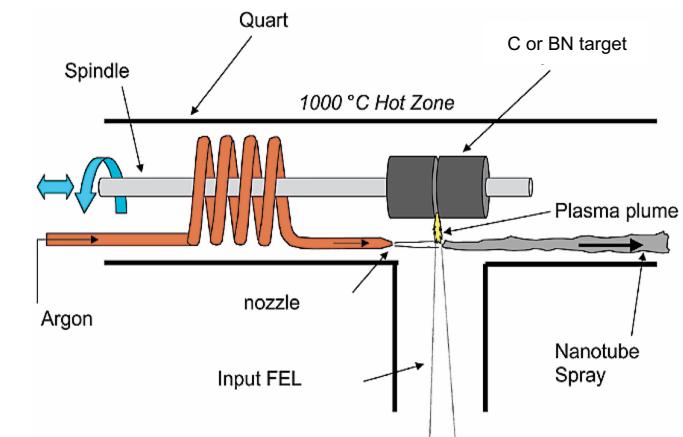


All Images Credit: NASA

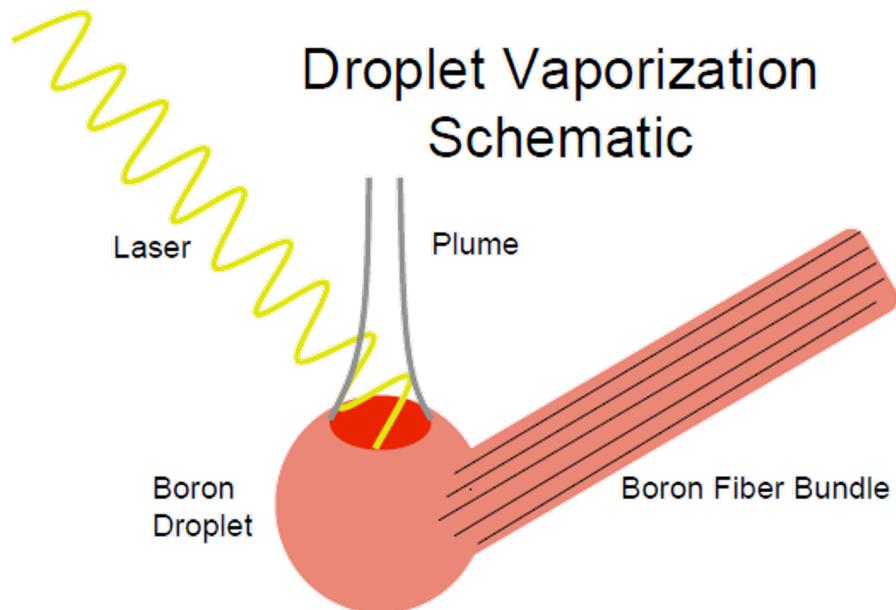
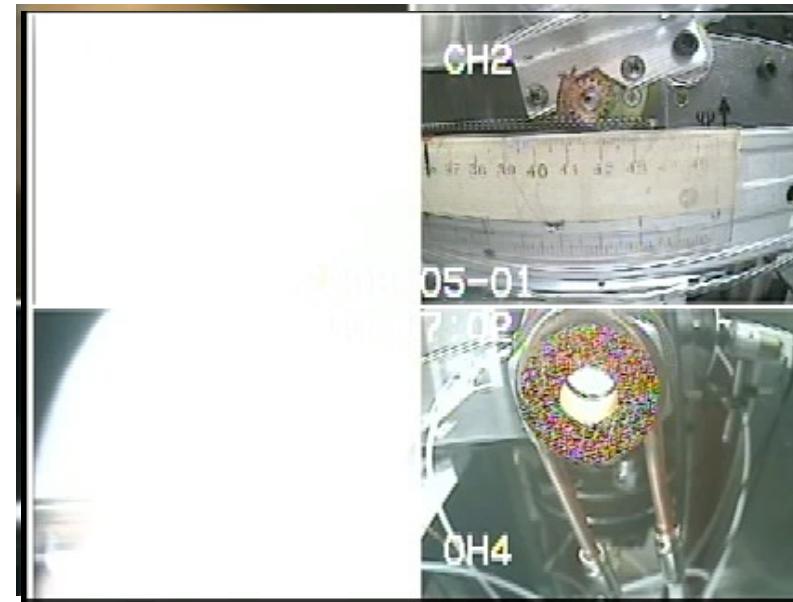
BNNT Synthesis

High Temperature-Pressure (HTP) BNNT

- Free Electron Laser (FEL) or CO₂ laser
- **No Catalyst, only B and N resource**
- Very long, small diameter, highly crystalline BNNT



BNNT Synthesis Lab: NASA Langley (1st Gen)

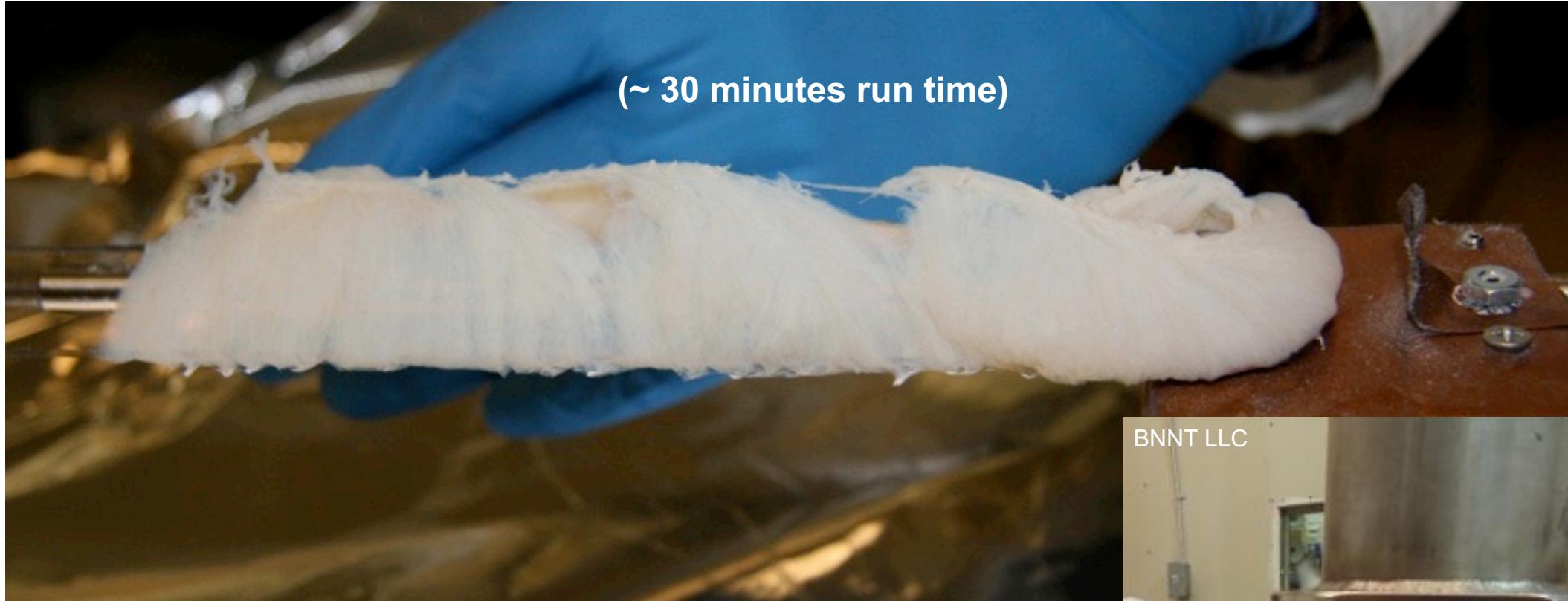


High Temperature Pressure (HTP) BNNT

- 5 kW of infrared radiation @ 10.6 μ m
- Heat source for vaporizing Boron feed stock above 3500°C
- Pressurized with Nitrogen to 13.6 atm (200 psi)

Nanotechnology, **20** 505604 (2009)
J. Thermophysics and Heat Transfer **27** 369 (2013)
Proc. SPIE **9060** 906006 (2014)

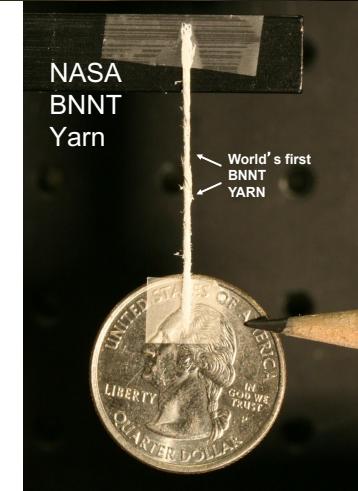
Cotton-like High Pressure and Temperature (HTP)-BNNT



BNNT LLC

Benefits

- One-to-few-walled tubes with high crystallinity
- Very long, high-aspect ratio tubes
- High scale-up potential
- No toxic catalysts (only B and N as reactants)
- Standard industrial cutting/welding lasers
- High service temperature (over 800°C)
- Highly electroactive (due to the B-N polar bond)
- Neutron radiation shielding (due to their B content)

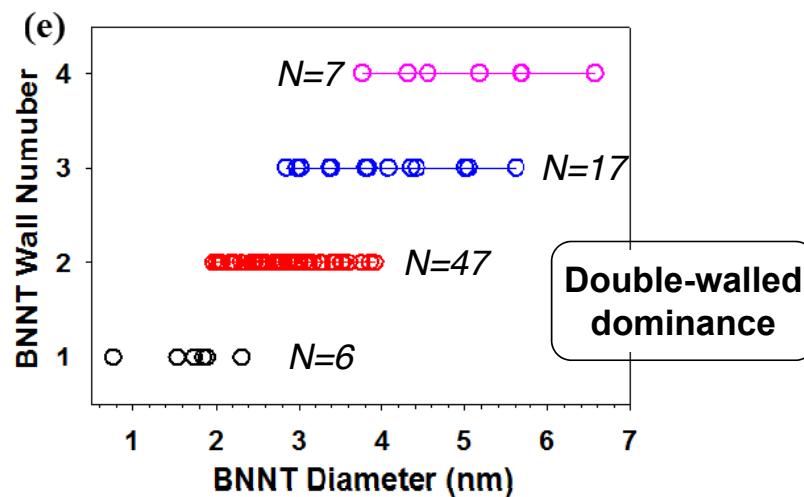
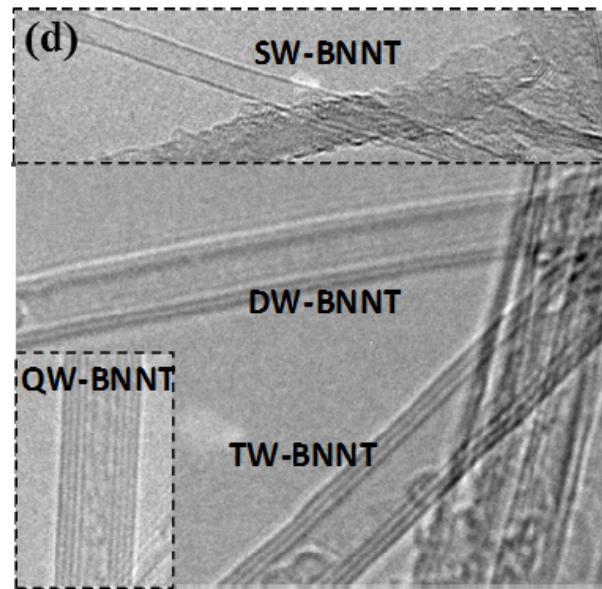


(From: M. W. Smith et al. Nanotechnology, 20, 505604 (2009))

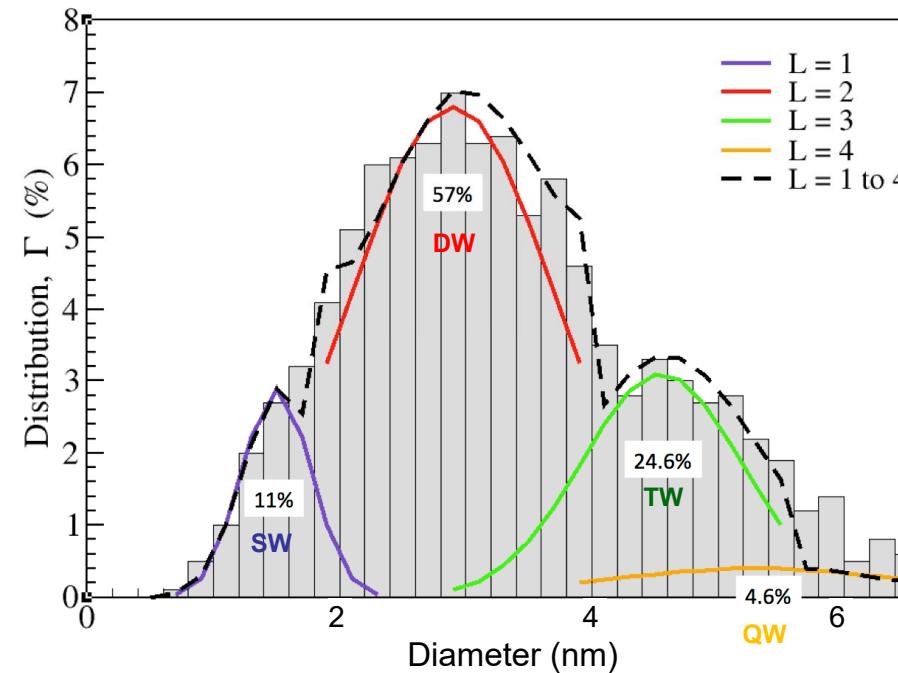


Nanotube Wall Number and Distribution of HTP-BNNTs

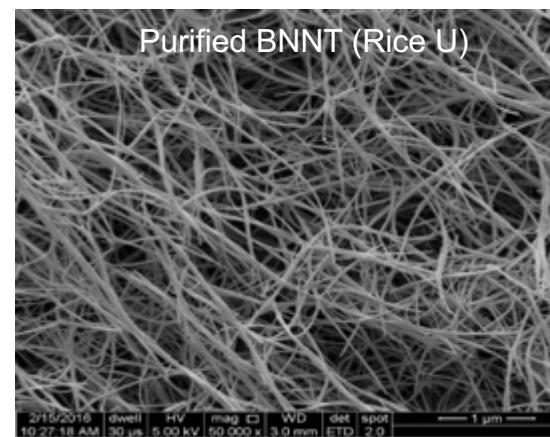
TEM Micrographs



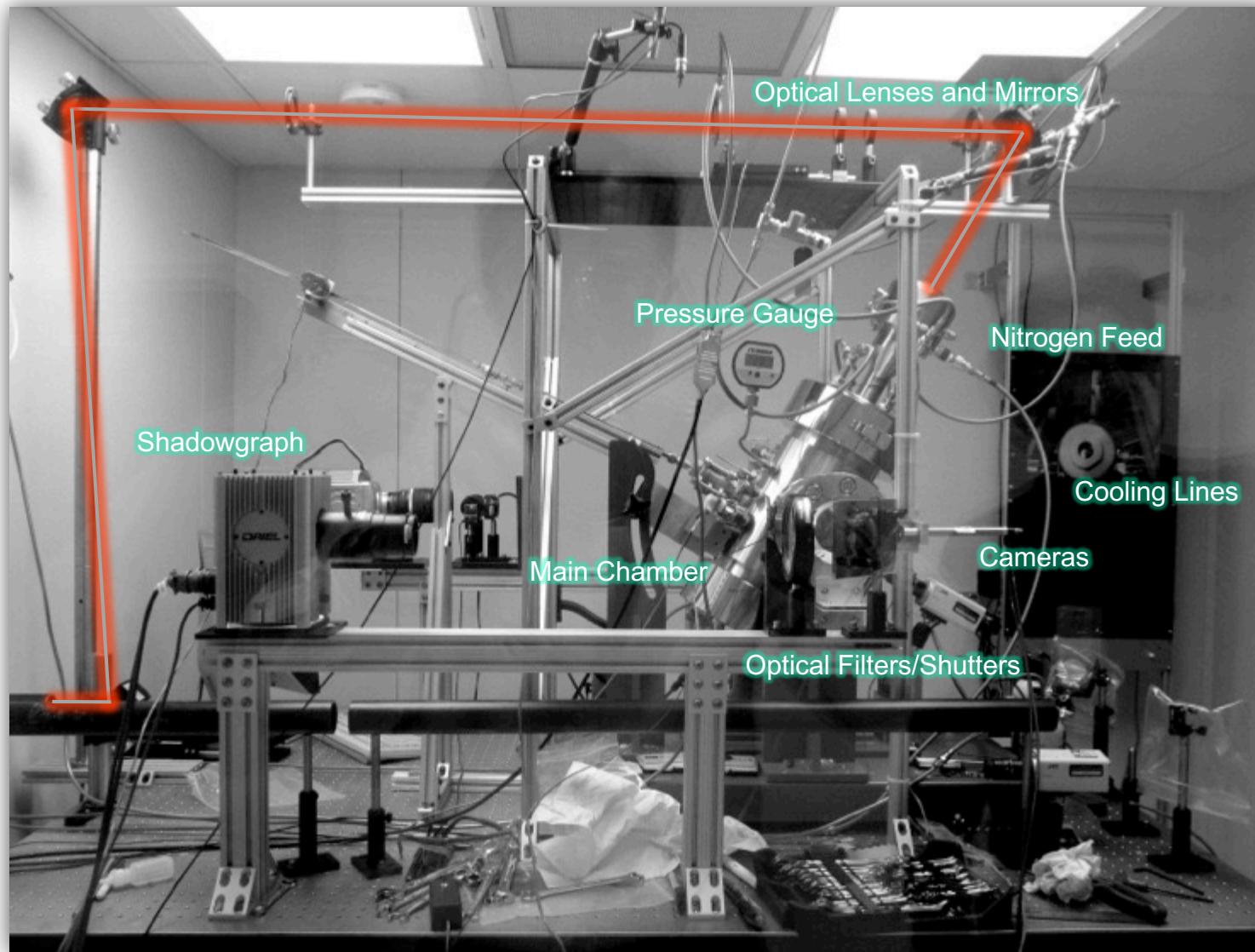
Based on AFM measurements of 1,000 randomly selected individual BNNTs



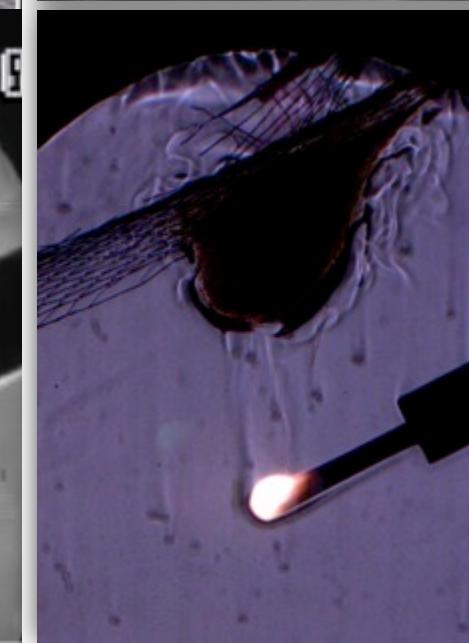
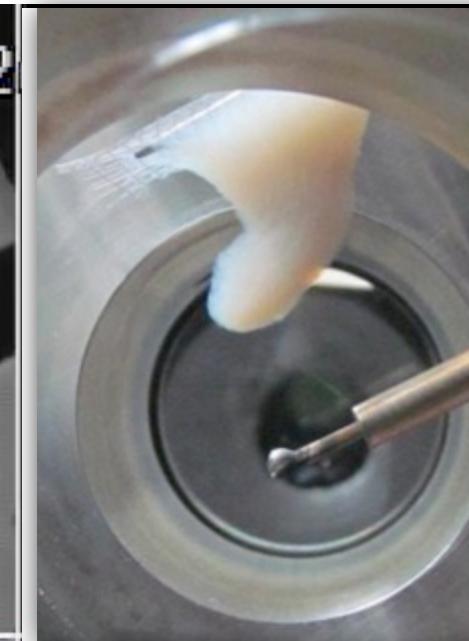
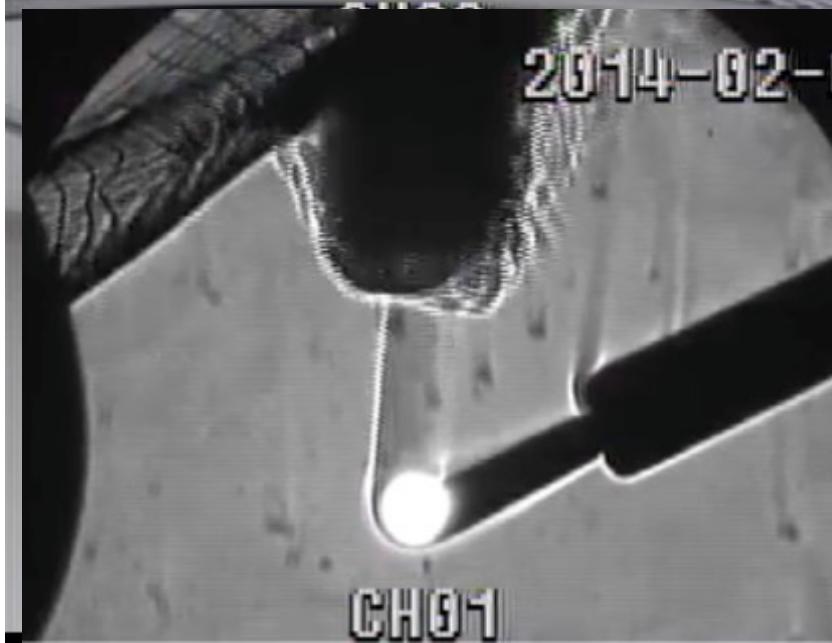
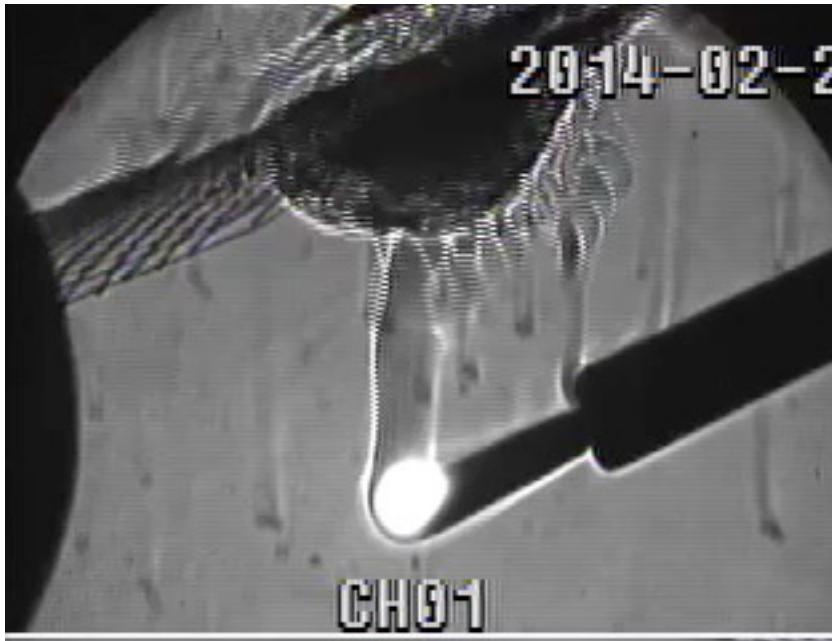
SW: 11%
DW: 57%
TW: 24.6%
QW: 4.6%
Total: 97.2%



National Institute of Aerospace (NIA) BNNT Science Chamber

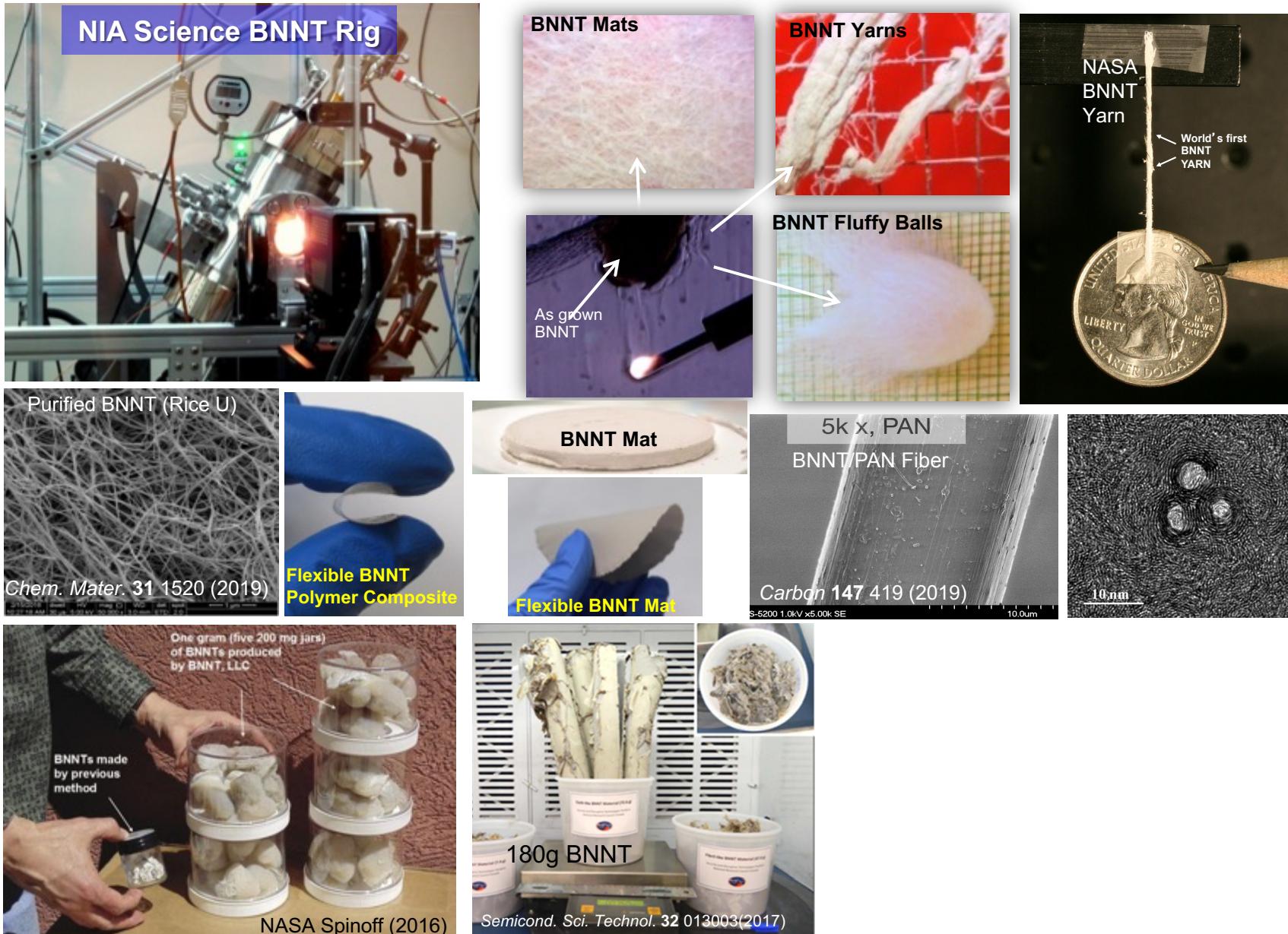


NIA Science Rig HTP BNNT Run (Snapshots)



All images credit: NASA/NIA

BNNT Scale-Up and Various Forms of BNNT





Dispersion and Purification

Thermodynamic Approach: Effective BNNT Dispersion

Essential for Quality Yarn, Fabric, and Composite Formation



Thermodynamic Approach:
Gibbs Free Energy of Mixing

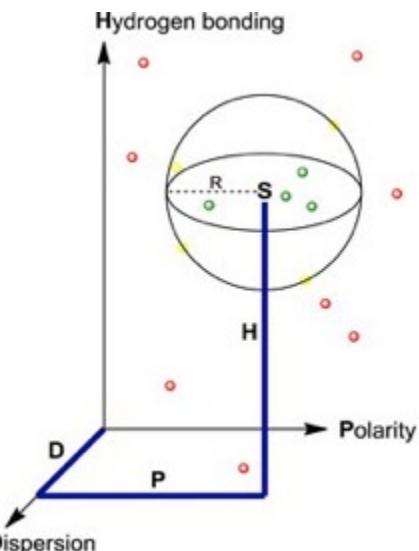
$$\Delta G_{mix} = \Delta H_{mix} - T^* \Delta S_{mix}$$

If ΔG_{mix} is negative,
spontaneous mixing happens
to form a homogeneous
solution

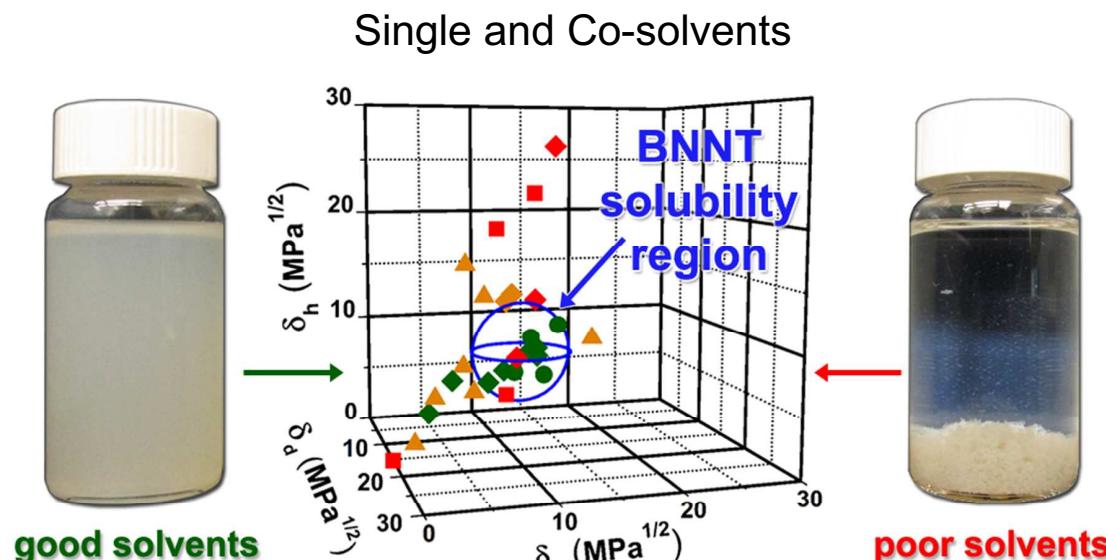
Hansen Solubility Parameters (HSP)
(d_d, d_p, d_h): "like dissolves like"

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

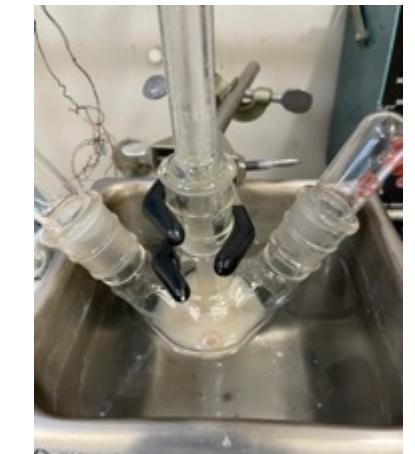
δ_t^2 : Hildebrand parameter
 d_d : dispersion component
 d_p : polar component
 d_h : hydrogen bonding component



Example of 3D Hansen space*



BNNT Hansen Solubility Parameters
 $\delta_d, \delta_p, \delta_h = 16.8, 10.7, 9.0 \text{ MPa}^{1/2}$
 $\delta_t = 21.8 \text{ MPa}^{1/2}$

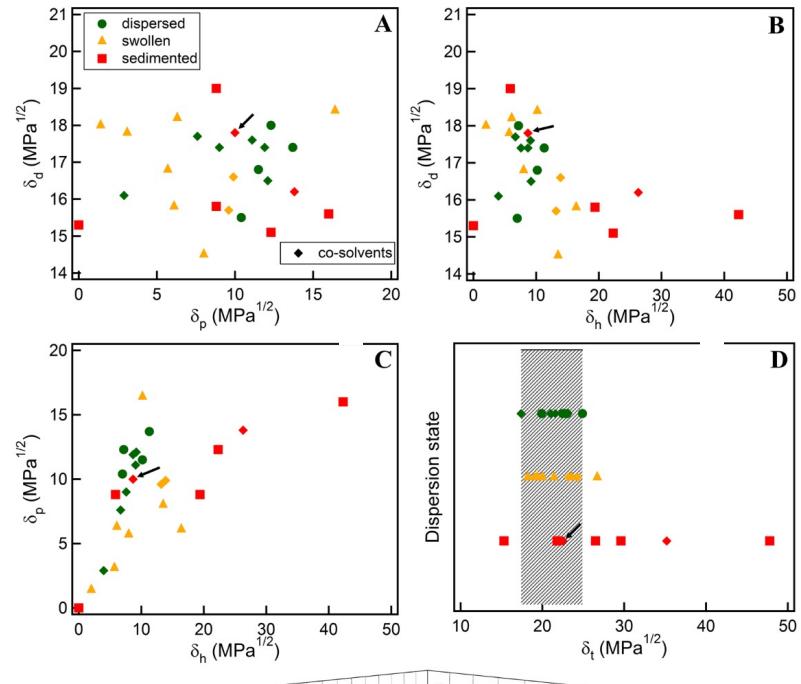
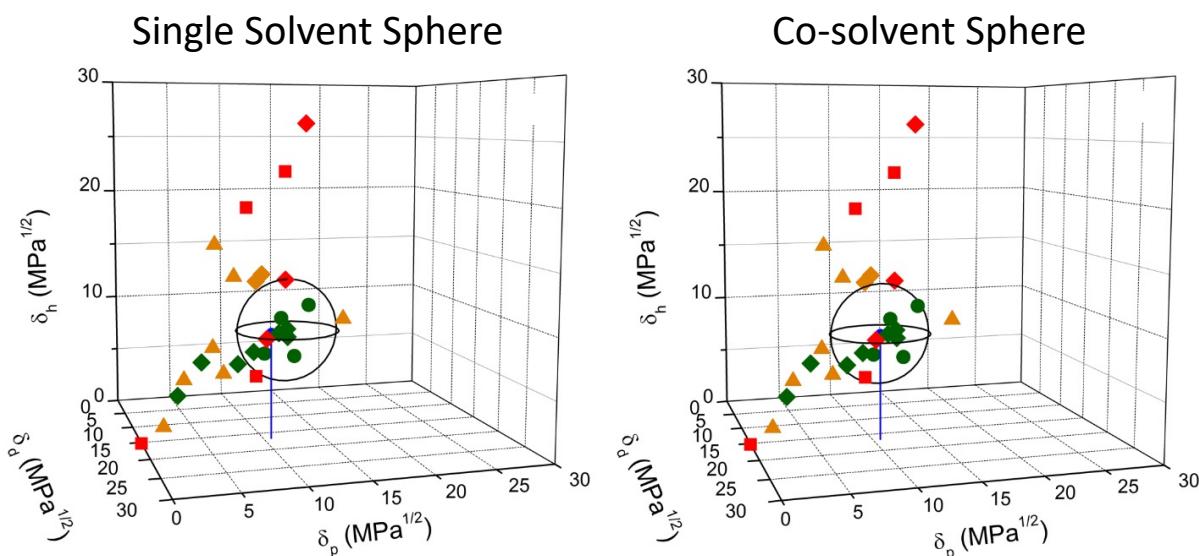


In-situ polymerization with BNNT
under shear and sonication

Dispersion: Dispersion State of Single and Co-solvents



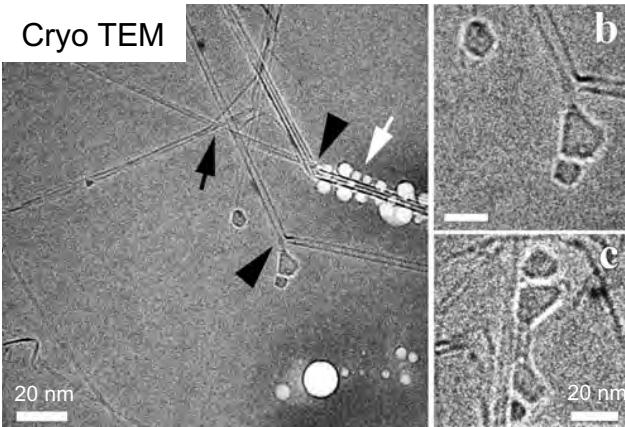
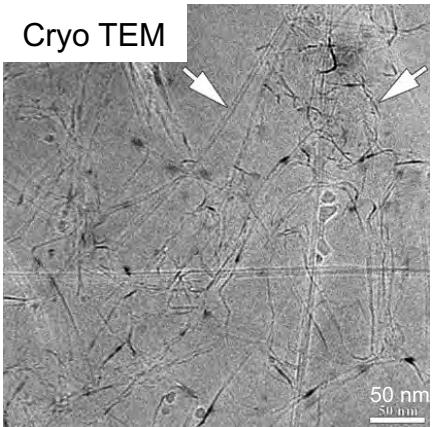
Co-solvent	δ_d , MPa $^{1/2}$	δ_p , MPa $^{1/2}$	δ_h , MPa $^{1/2}$	δ_t , MPa $^{1/2}$	Dispersion state (stirring only)	Dispersion state (stirring + 30 mins sonication)	R_a^c	RED^d
THF-NMP	17.4	9.0	7.6	21.0	swollen	dispersed/swollen ^b	2.51	0.58
DMF-acetone	16.5	12.1	9.2	22.4	swollen ^a	dispersed/swollen ^b	1.54	0.36
DMAc-NMP	17.4	11.9	8.7	22.8	swollen ^a	dispersed/swollen	1.72	0.40
DMSO-THF	17.6	11.1	9.1	23.1	swollen	dispersed/swollen ^b	1.65	0.38
DMF-toluene	17.7	7.6	6.7	21.6	swollen	dispersed	4.26	0.99
IPA-DMF	16.6	9.9	13.9	24.3	sediment	dispersed/swollen ^b	4.98	1.16
ethanol-acetone	15.7	9.6	13.2	23.2	swollen	dispersed/swollen ^b	4.87	1.13
DMF-DCM	17.8	10.0	8.7	22.5	swollen	dispersed/swollen ^b	2.14	0.50
THF-hexane	16.1	2.9	4.0	17.4	sediment	dispersed/swollen	9.37	2.18
DMAc-water	16.2	13.8	26.3	35.2	swollen	sediment	17.62	4.10



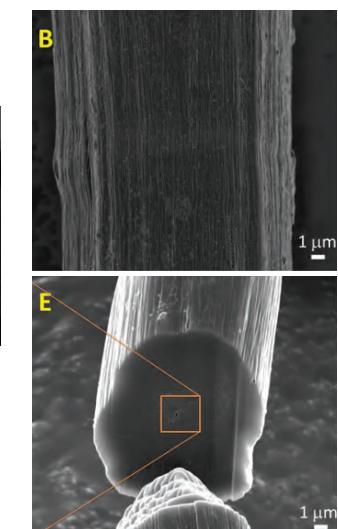
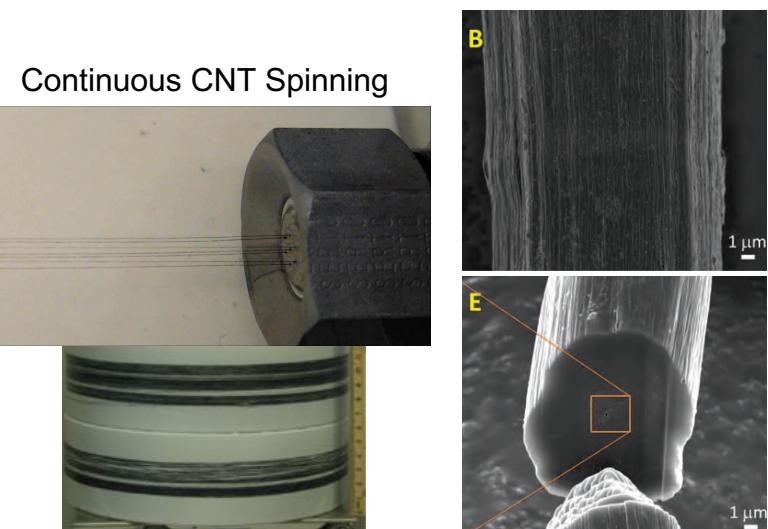
BNNT HSP
 $\delta_d, \delta_p, \delta_h = 16.8, 10.7, 9.0 \text{ MPa}^{1/2}$
 $\delta_t = 21.8 \text{ MPa}^{1/2}$

Dispersion and Purification

Dispersion in a Superacid (Chlorosulfuric acid)



BNNT in Chlorosulfuric acid (HSO_3Cl)



Rice U Nanotube Spinning (*Science* **339** 182 (2013))

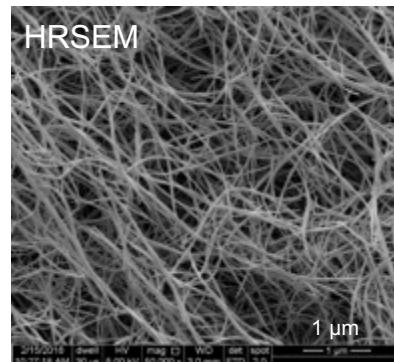
Purification: Wet Thermal Oxidation



As grown BNNT



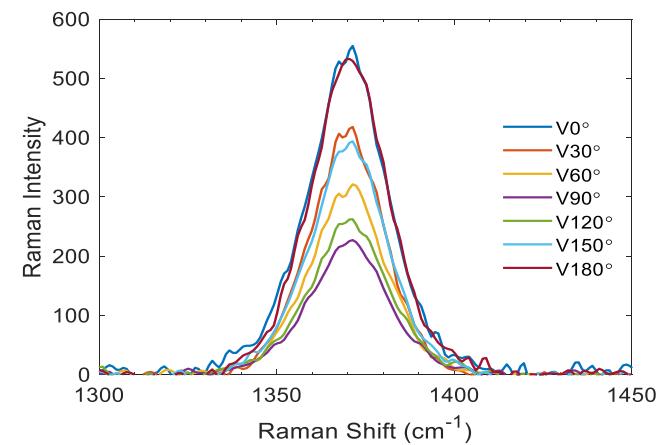
Purified BNNT



Purified BNNT



Raman: Degree of Alignment

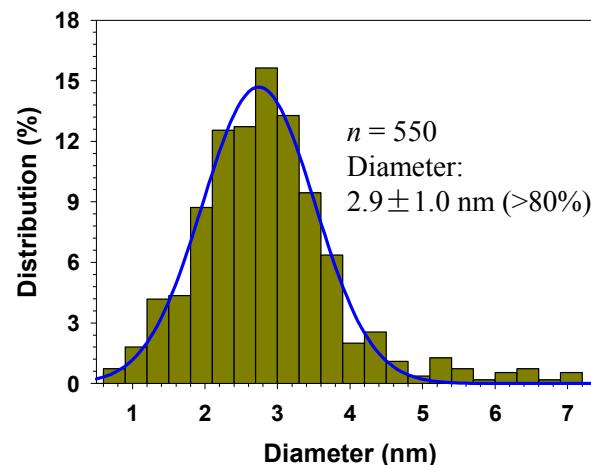
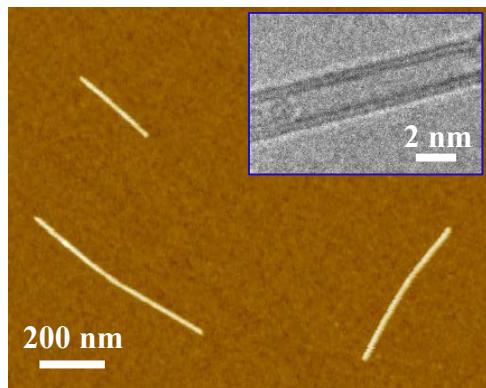




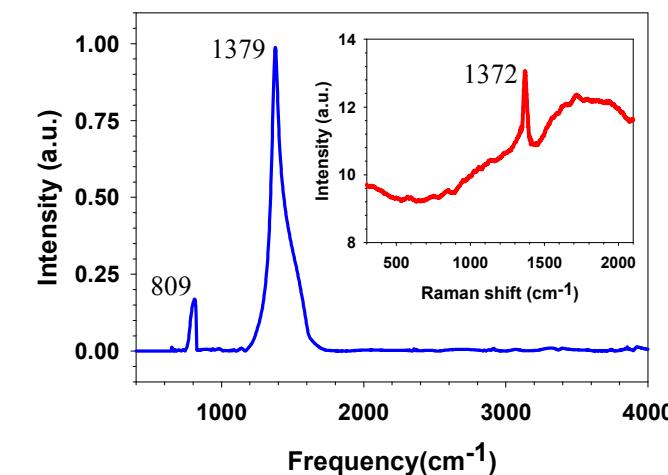
Mechanical and Thermal Properties

In-situ Single BNNT Test inside of an SEM

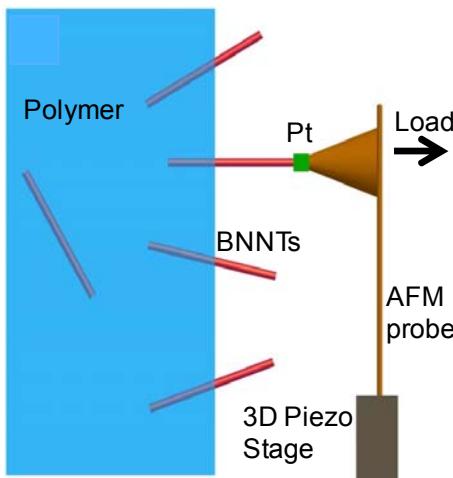
AFM



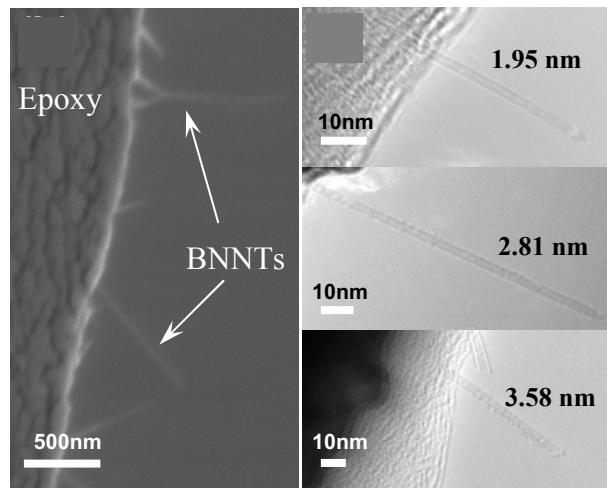
FTIR and Raman



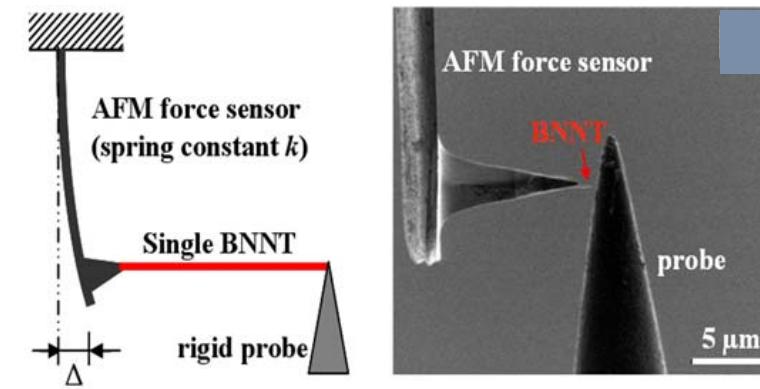
Pull-Out Test



SEM

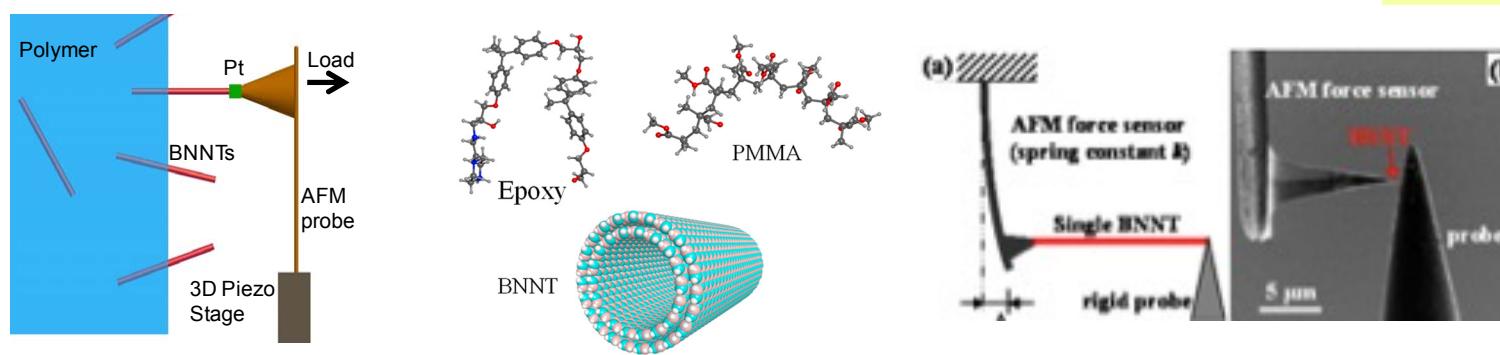
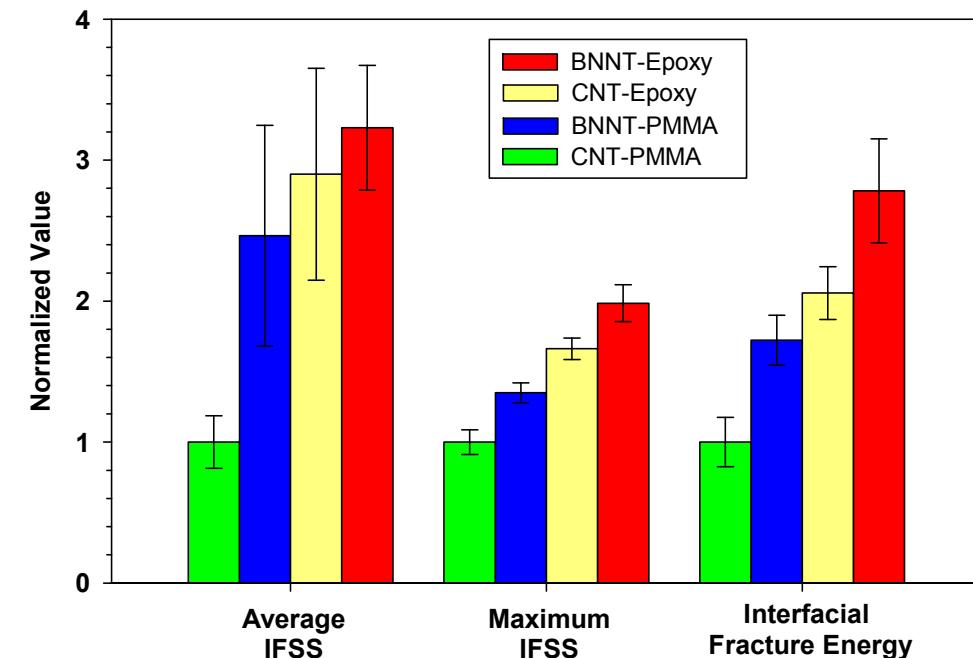
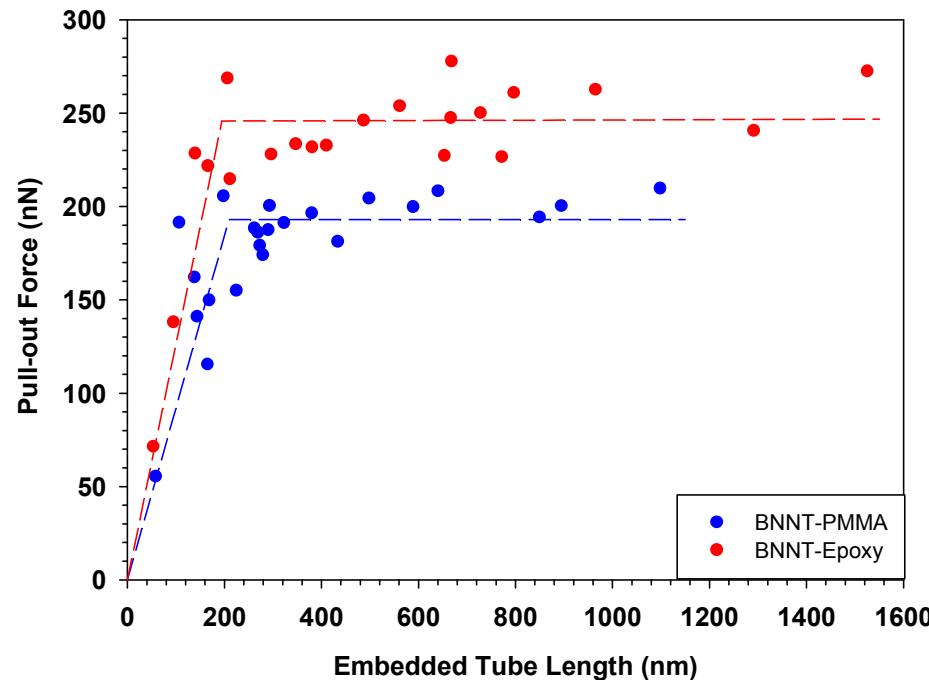


Tensile Test



Small **9** 3345 (2013), *Carbon* **82** 214 (2015), *APL* **107** 253105 (2015)
Carbon **25** 93 (2017), *Carbon* **132** 548 (2018), *Nanotechnology* **30** 025706 (2019)

Interfacial Strength: *In-situ* Single Nanotube Pull-Out Test



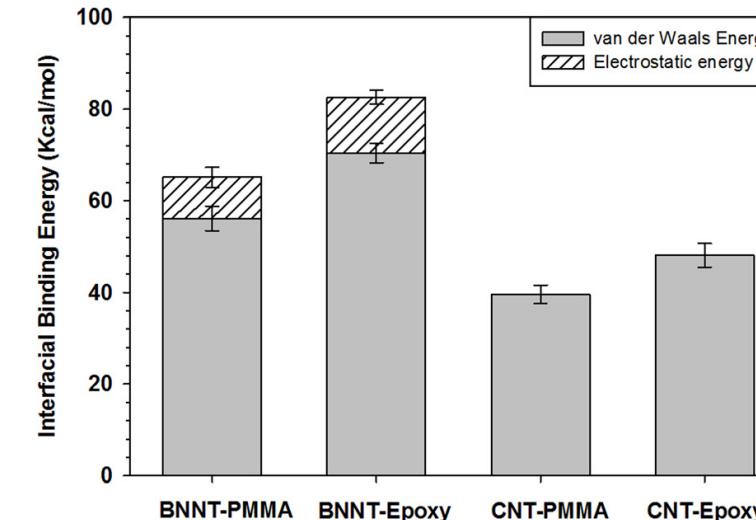
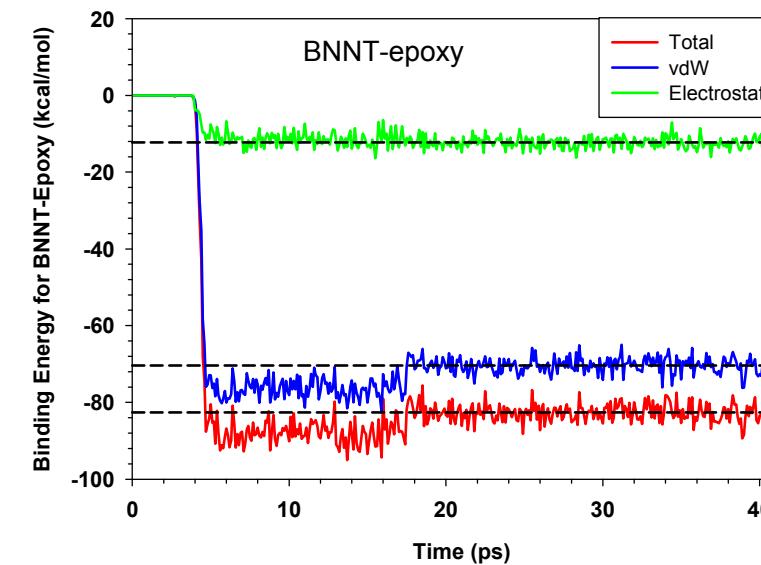
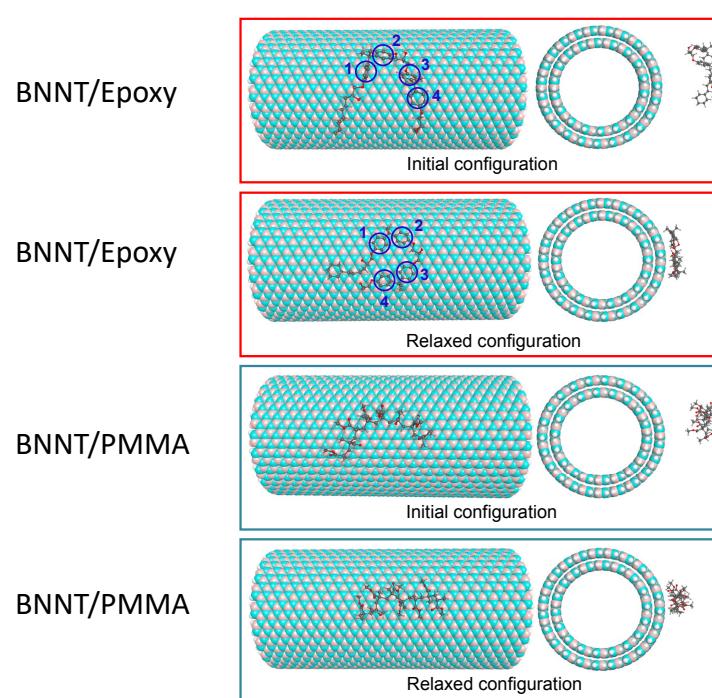
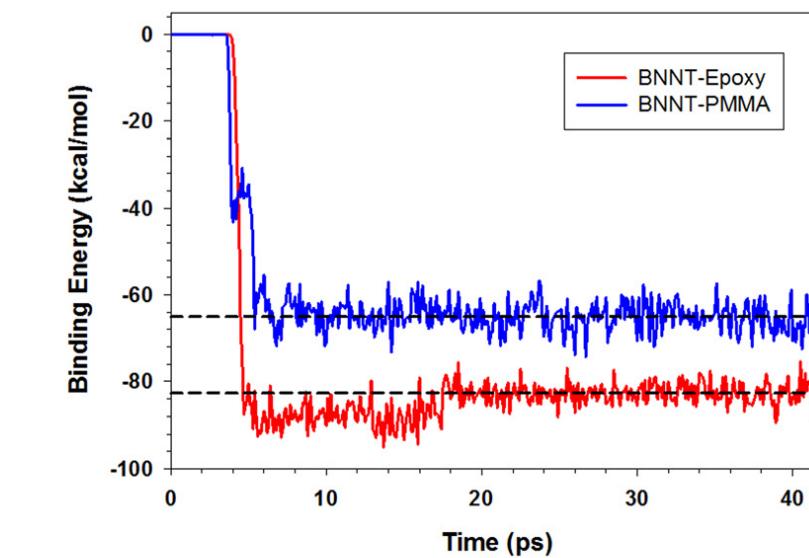
Interfacial strength of BNNT is superior to that of CNT

BNNT Tensile Test Results

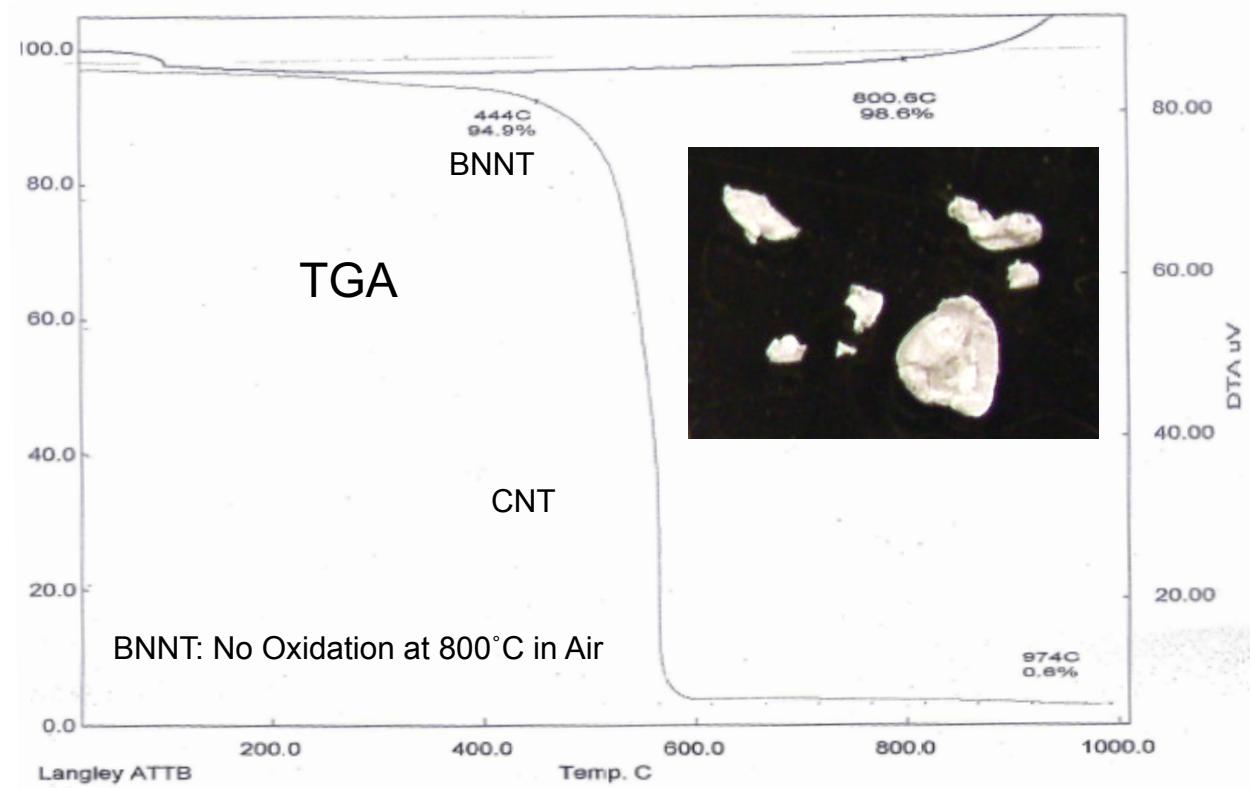
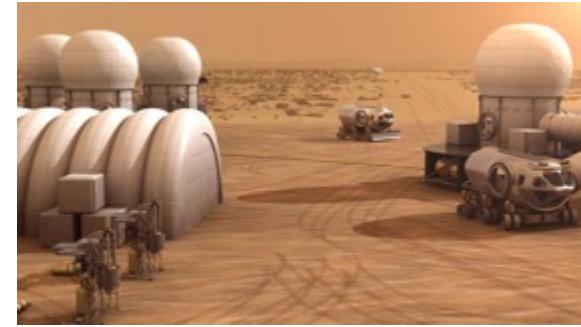
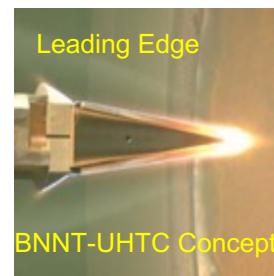
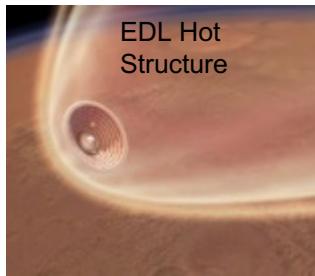
Diameter	Elastic modulus (GPa)	Breaking Strength (GPa)
D = 2.5 nm	760-960	14-38

Interfacial Strength: *In-situ* Single Nanotube Pull-Out Test

Credit: Prof Ke (SUNY Binghamton)



Thermal Properties of BNNT



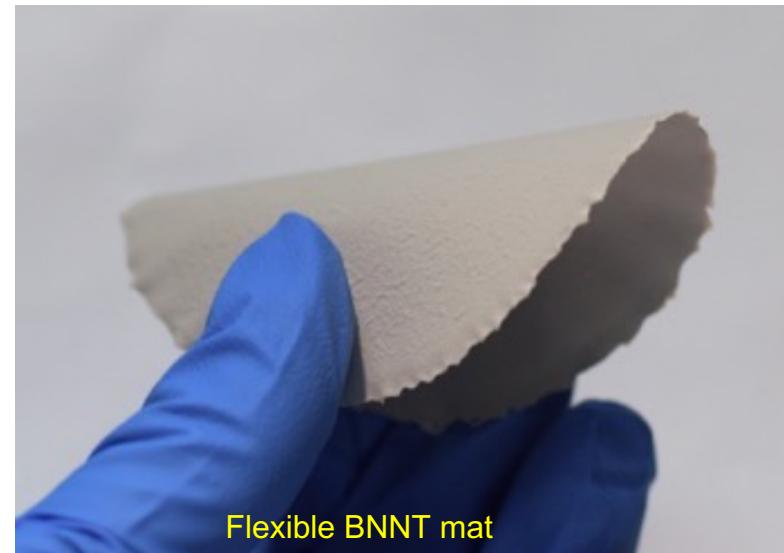
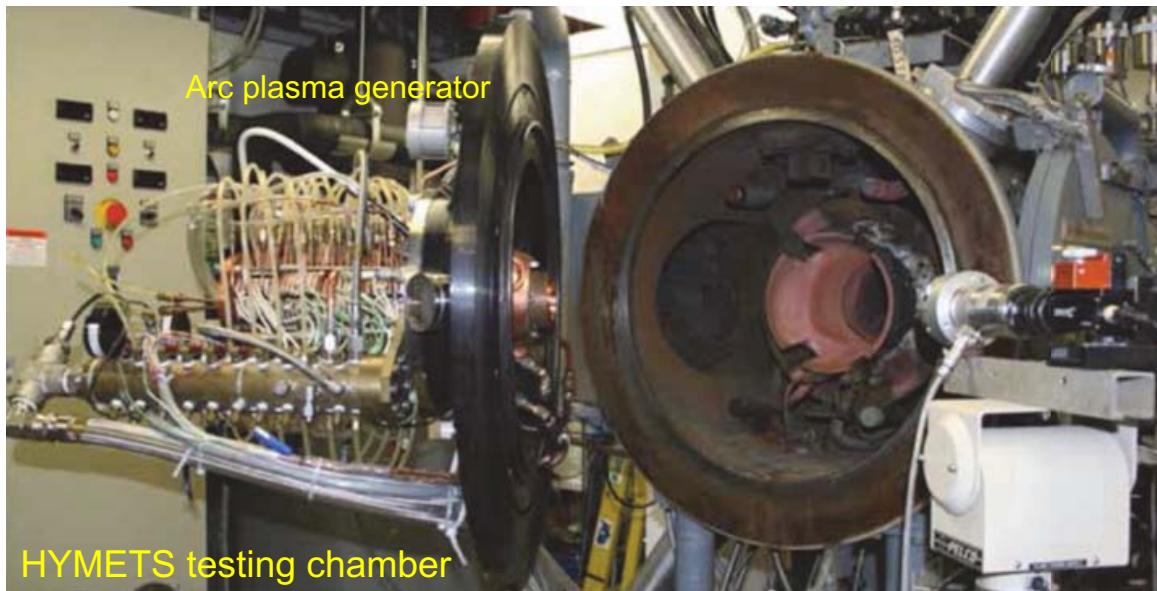
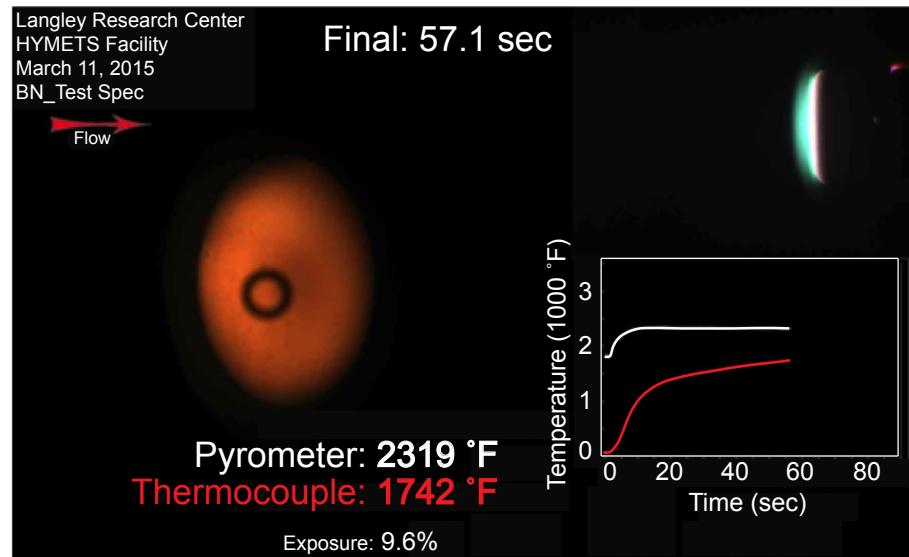
Hypersonic Materials Experiment Test System (HyMETS)

LaRC HYMETS Test Conditions

- Specimen Surface Temperature (°C): 1260
- Specimen Stagnation Pressure (atm): 0.013-0.079
- Free Stream Mach Number: 5.0
- Free Stream Enthalpy (kJ/kg): 5350-26749

HYMETS TEST for BNNT Mats

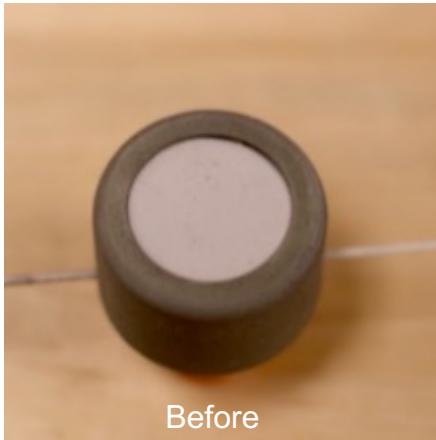
- Heat flux: Set at **50 W/cm²** (**2nd Gen Mars EDL**)
- Duration: 1 min - 5 min
- Atmosphere: Air (with 5% Ar)
- Cooled under Vacuum



Hypersonic Materials Experiment Test System (HYMETS)

Sample: BNNT Mat (as grown, nonwoven)

- Fabricated by a vacuum filtration process
- Diameter: 25 mm, Thickness: 2 mm, Density: $\sim 0.3 \text{ g/cm}^3$



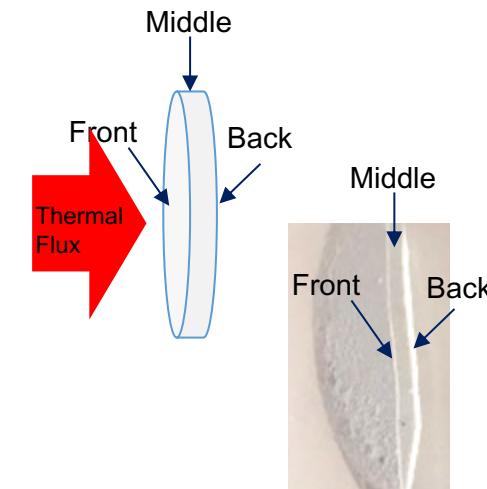
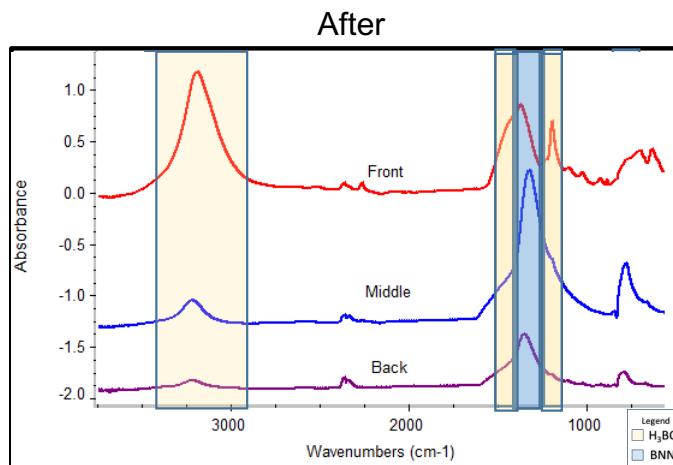
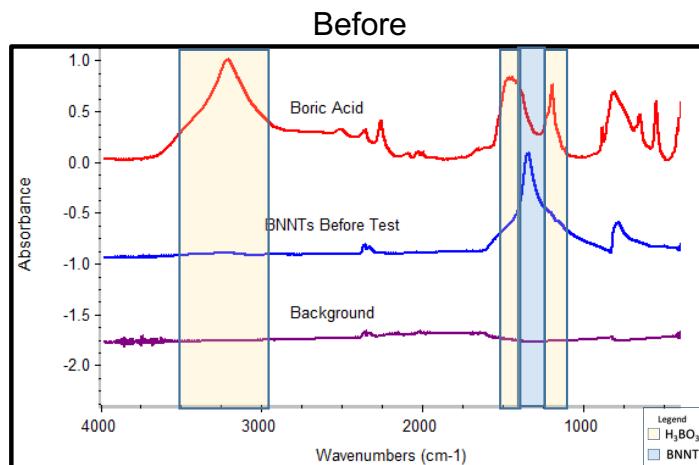
HYMETS Test Conditions

- Test duration: 1 min
- Surface temperature: 2400 °F (1315 °C)

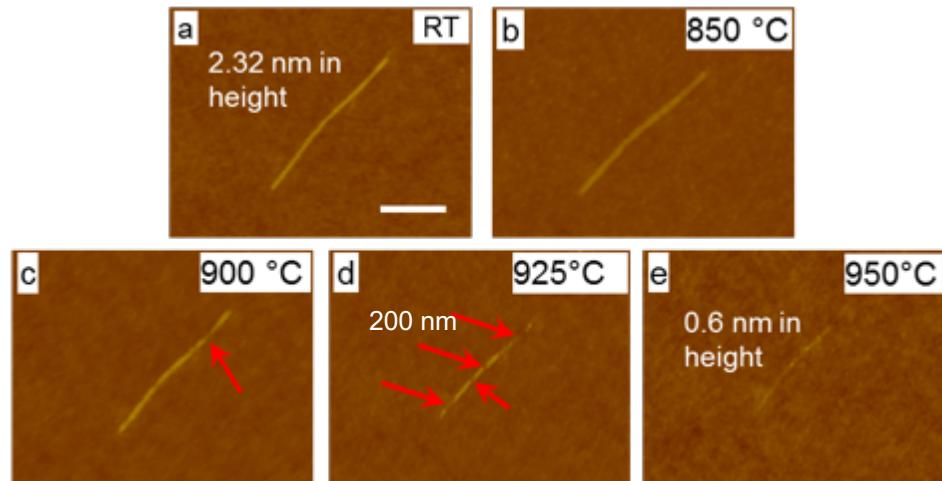


Video Clip: BNNT mat under a hypersonic test

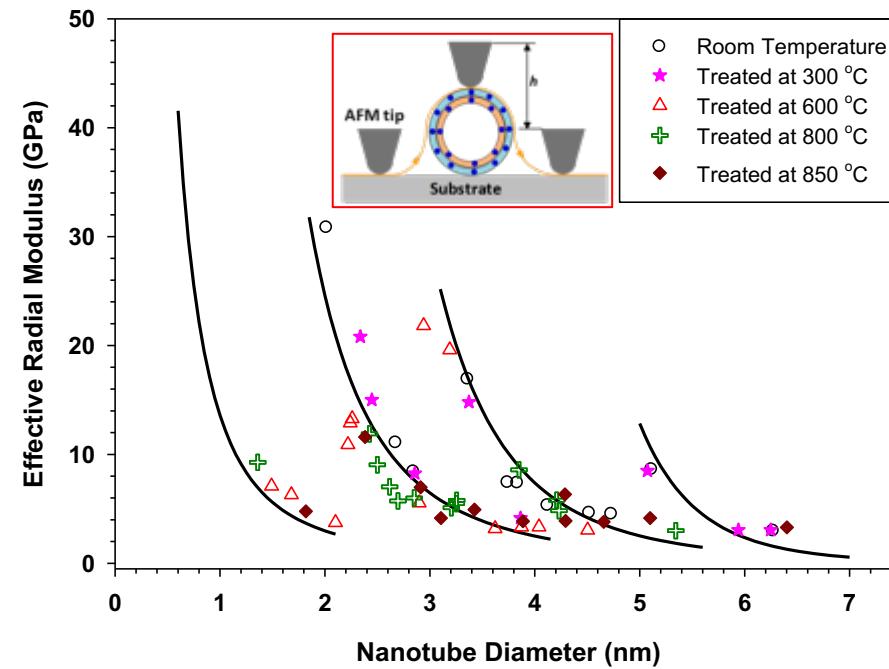
FT-IR Analysis of BNNT mat



Superior Structural and Mechanical Properties of BNNTs in High Temperature Environments

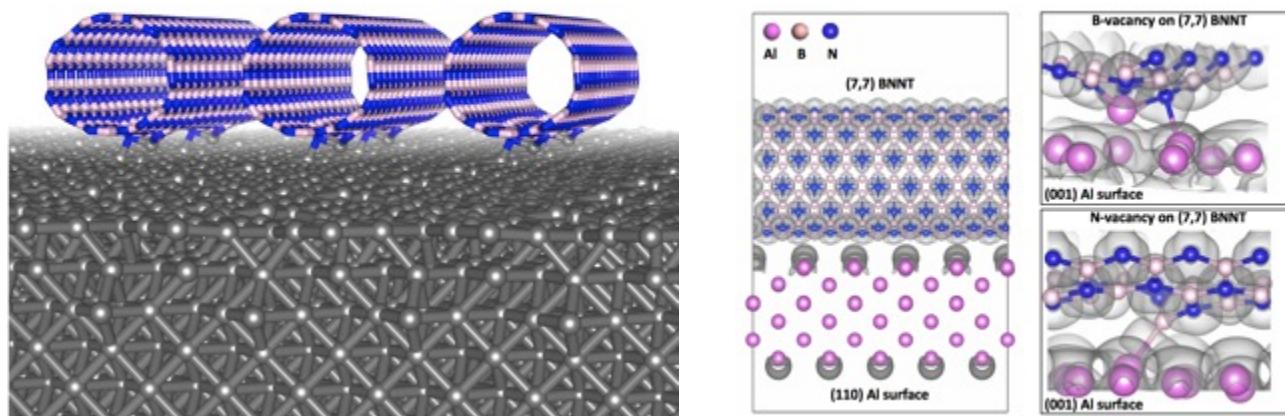


AFM studies show that individual BNNTs can survive at up to 850 °C in air and captures the sign of their structural degradation at 900 °C and above. (the red arrows mark the positions of the oxidation-induced tube broken sites).



AFM-based nanomechanical compression tests (illustrated in inset drawing) show that the mechanical properties of individual BNNTs remain intact after thermally baked at up to 850 °C in air.

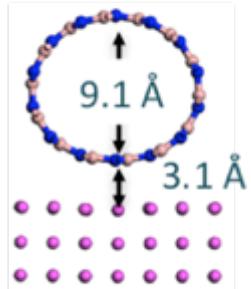
BNNT Metal Matrix Composite (MMC) BNNT Ceramic Matrix Composite (CMC)



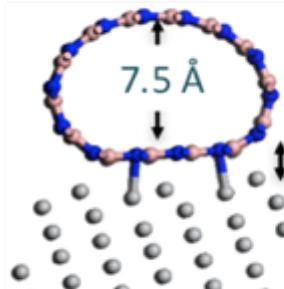
BNNT Metal Matrix Composite (BNNT-MMC)



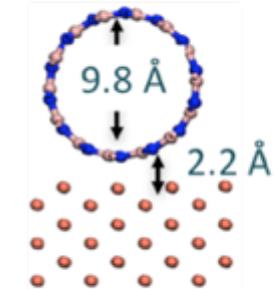
Pristine BNNT (7, 7)



Al [100] surface



Ti [111] surface

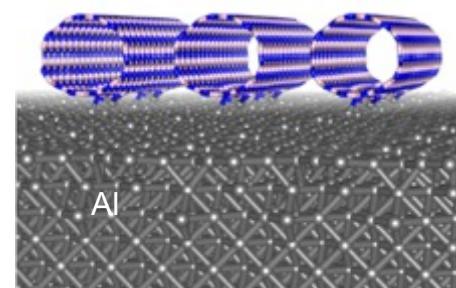


Cu [110] surface

U Queensland: Prof Bernhardt & Dr. Rhomann (AFOSR/AOARD)

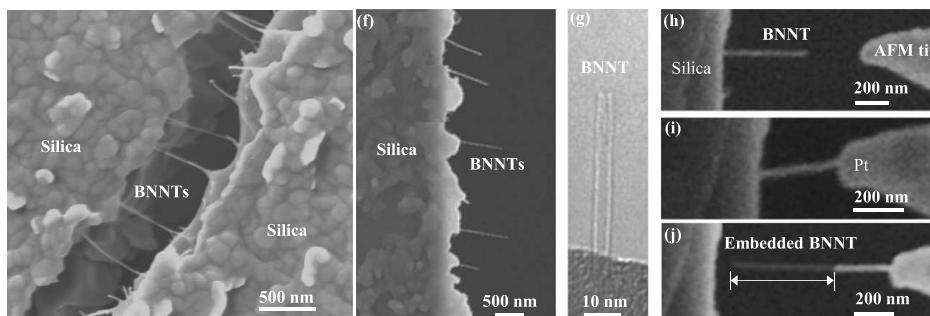
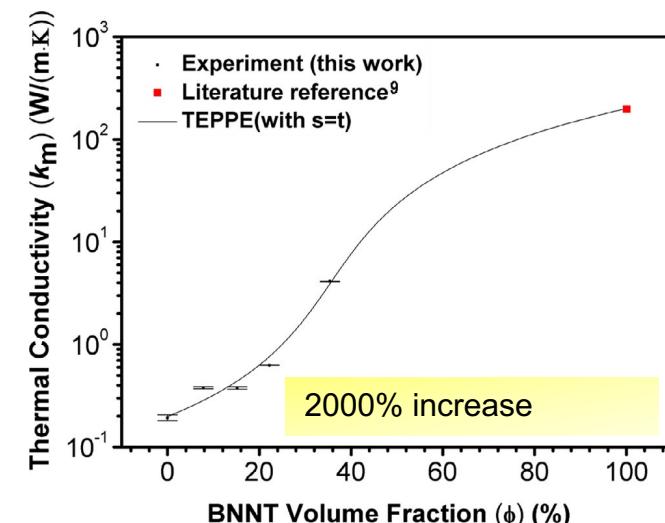
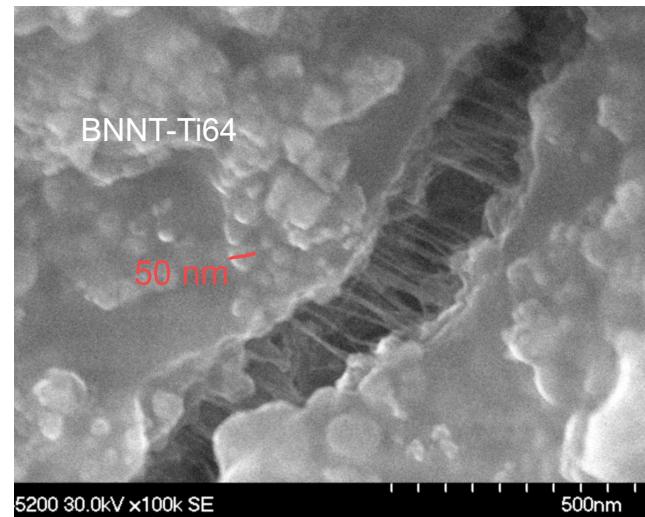
Binghamton U: Prof Ke group (AFOSR)

- B
- N
- Al
- Ti
- Ce



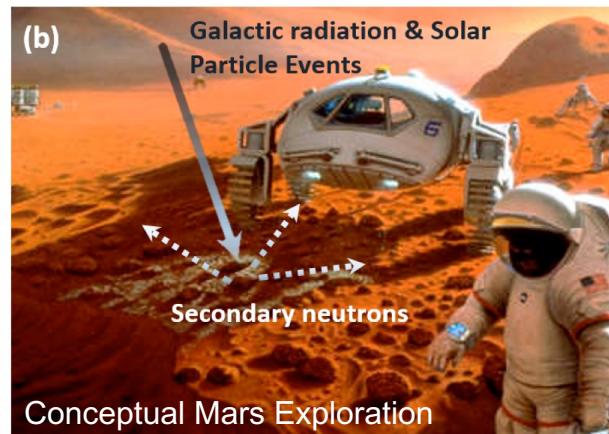
Interfacial strengths of BNNT are superior to that of CNT in **PMC**, **CMC**, and **MMC**.

Binding Energies ^{**}	Al[100] Surface	Ti[111] Surface	Cu[110] Surface
Pristine	-0.41	-1.77	-0.95
N-vacancy	-0.69	-2.00	-1.23
B-vacancy	-1.26	-3.30	n/a
C sub N	-0.64	-2.17	-1.26
C sub B	-0.51	-1.41	-1.00



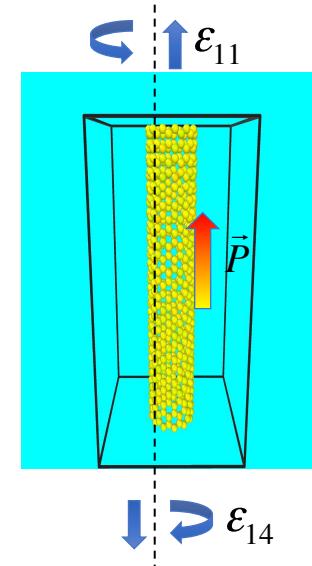
Multifunctional BNNT Polymer Composites

- Electroactive Properties
- Radiation Shielding Properties



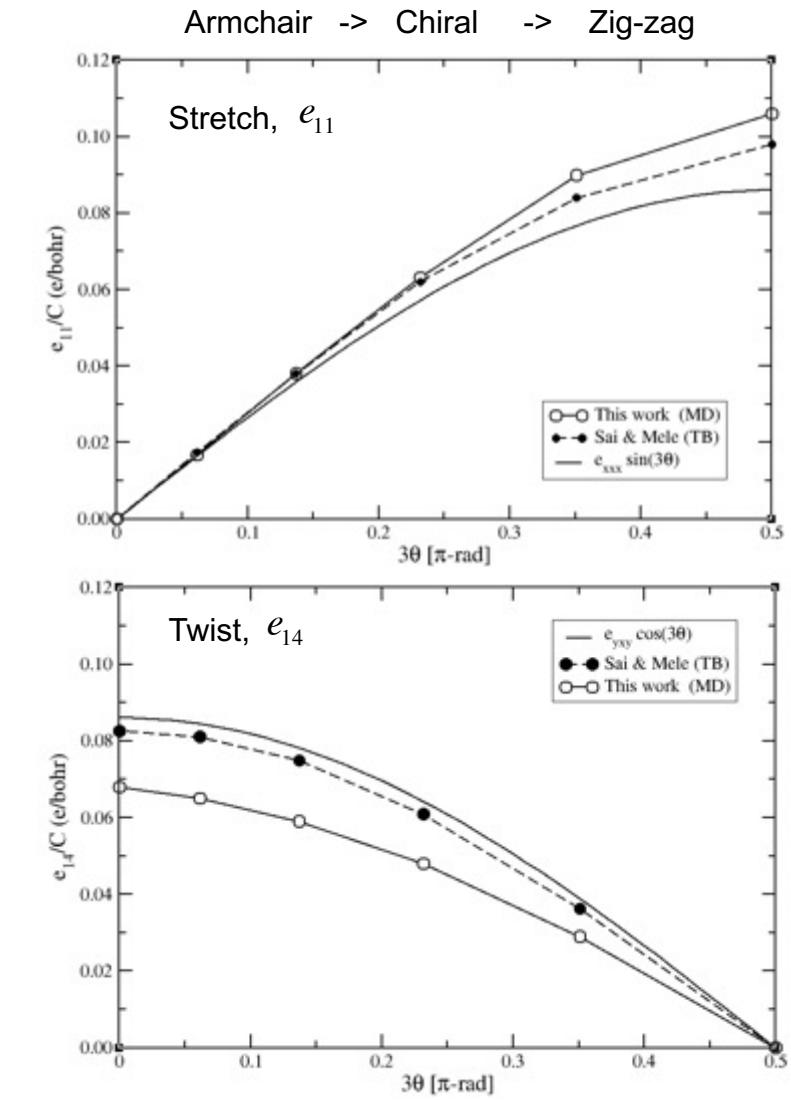
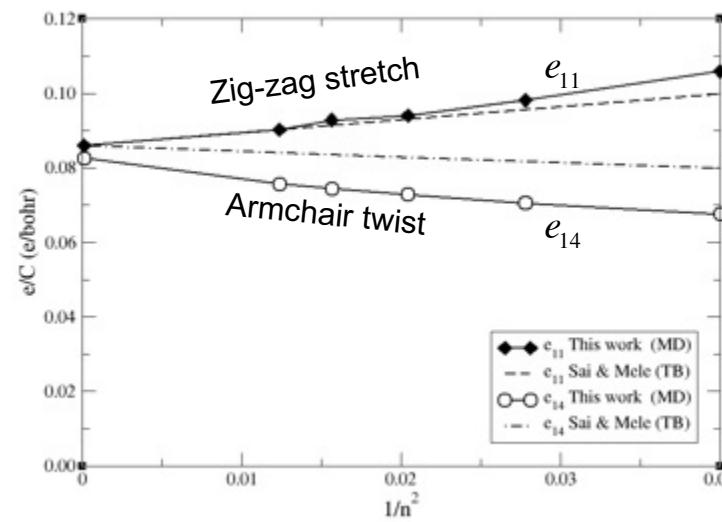
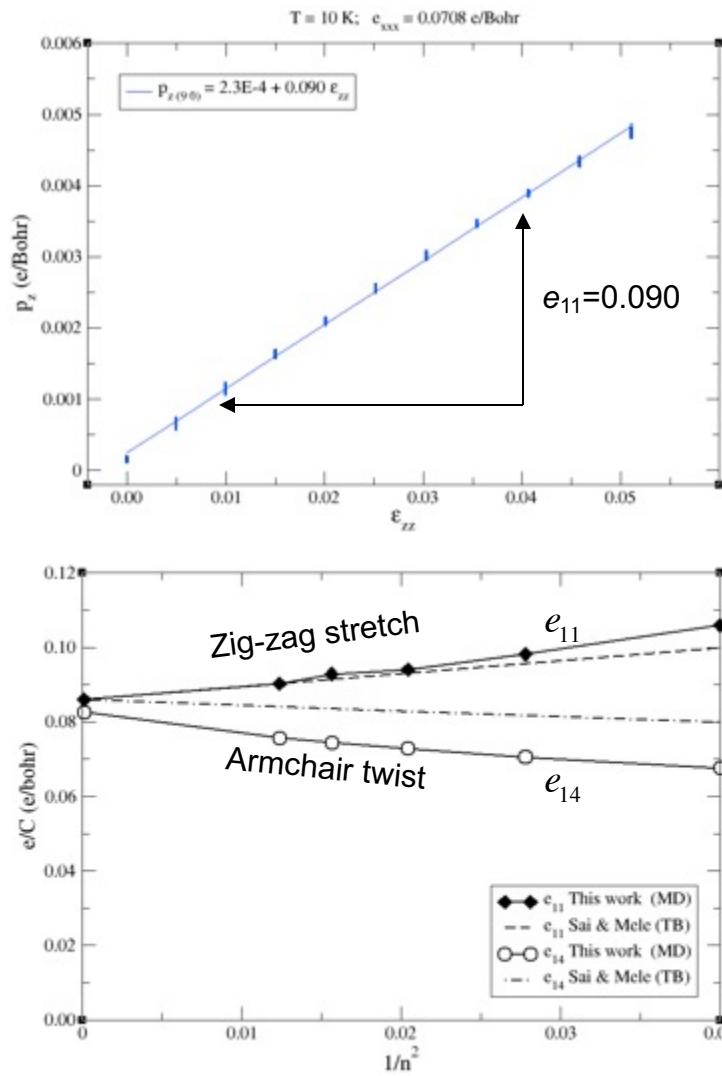
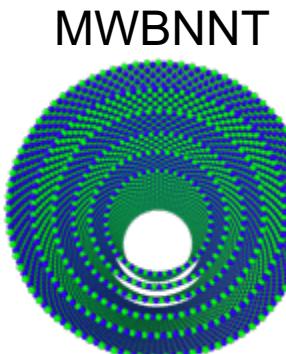
Results: Piezoelectricity under Deformation

The Molecular Dynamics (MD) model is successful in representing the piezoelectric properties of BNNTs

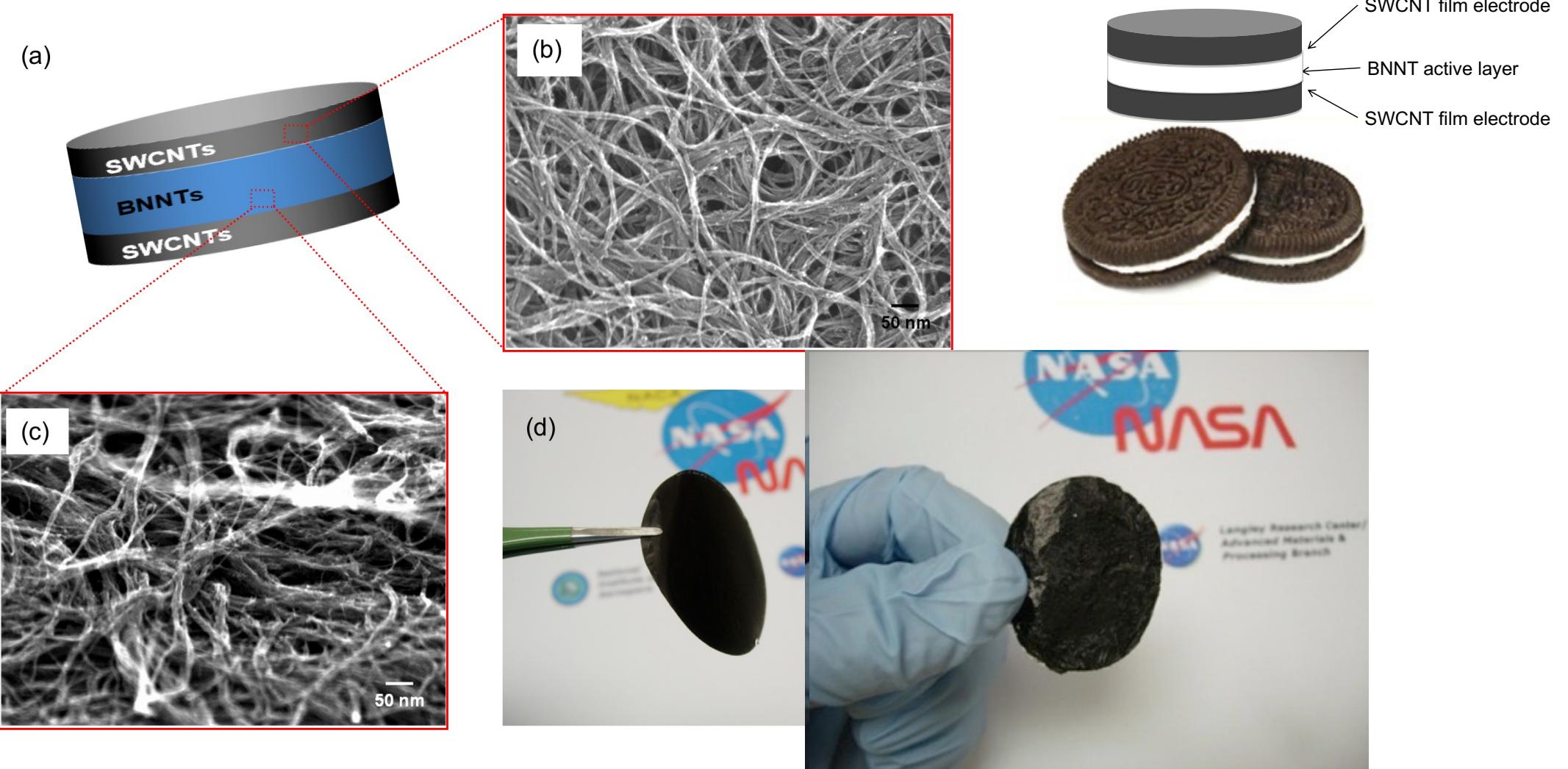


$$p_z(\text{stretch}) = e_{11} \varepsilon_s$$

$$p_z(\text{twist}) = e_{14} \varepsilon_t$$

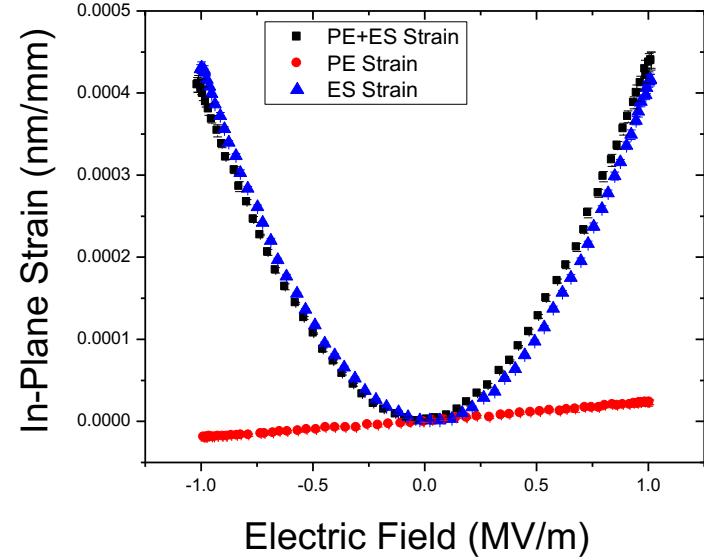


Langley All-Nanotubes Actuator/Sensor (LaRC-ANAS) Film



Goal: Flexible, transparent, large actuation, high sensitivity, mechanically durable

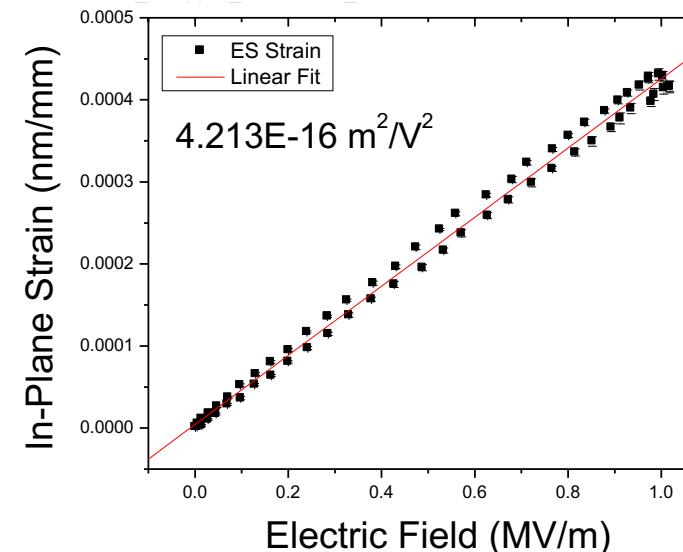
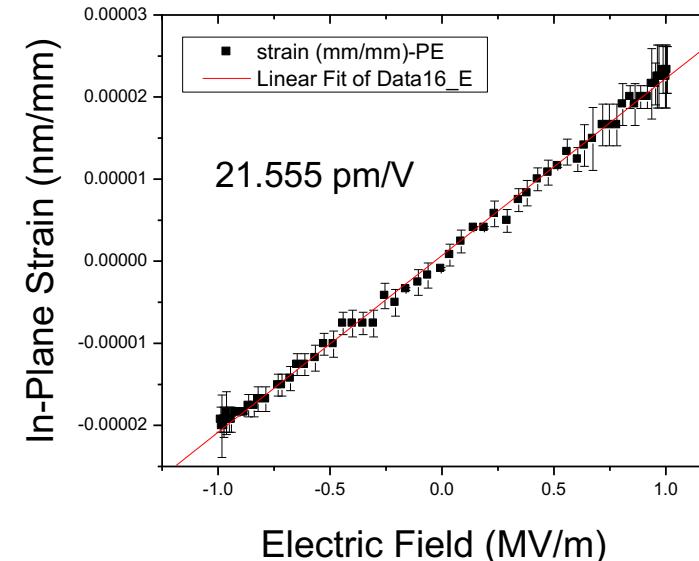
All-Nanotubes Actuator/Sensor Film: In-Plane Strain



Field induced strain (e_{33})

$$e_{33} = d_{33} \cdot E + M_{33} \cdot E^2 + \dots$$

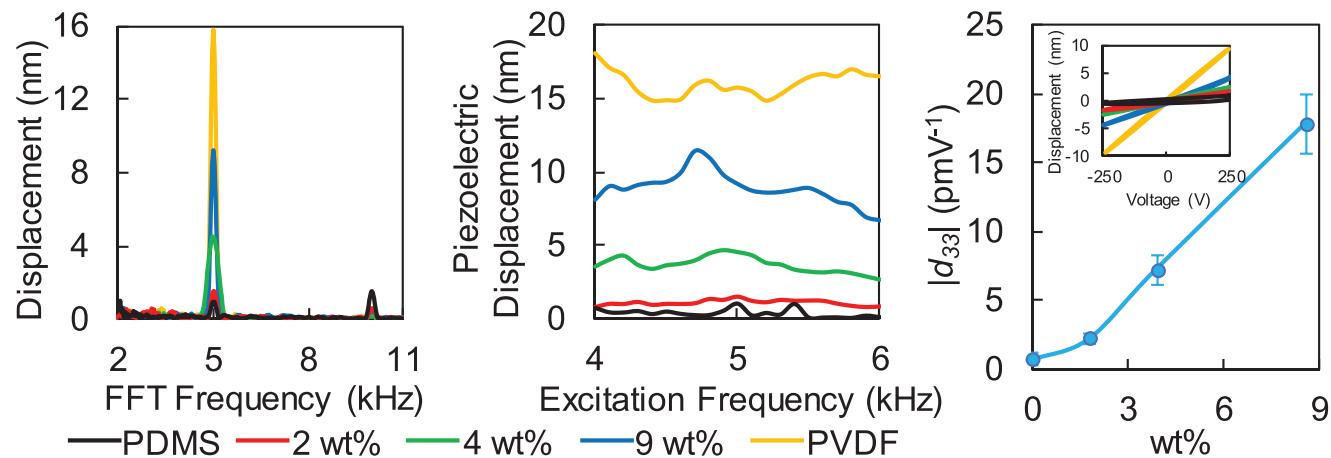
d_{33} : piezoelectric coefficient
 M_{33} : electrostrictive coefficient
 E : applied electric field



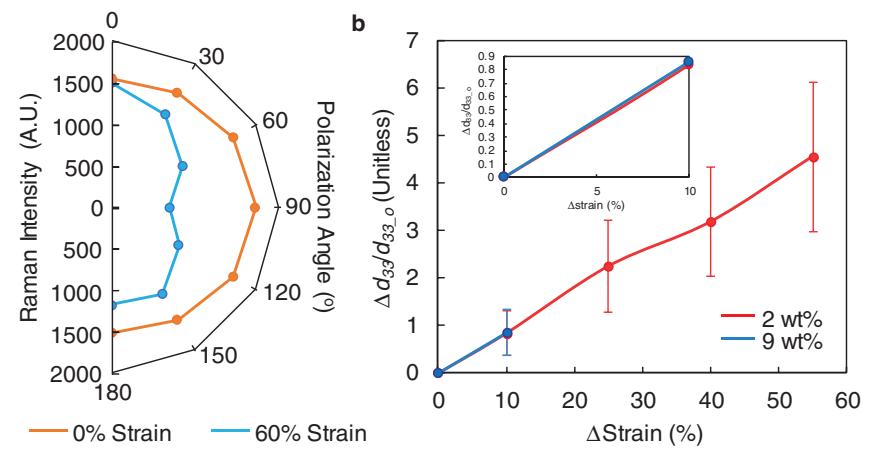
Multifunctional Properties of BNNT/PDMS (Poly(dimethylsiloxane))



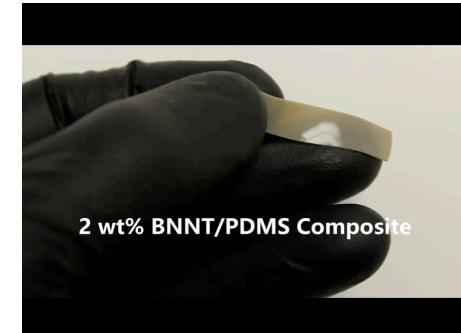
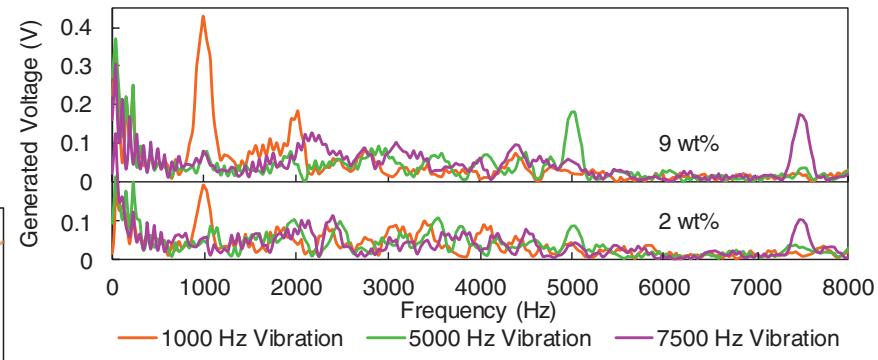
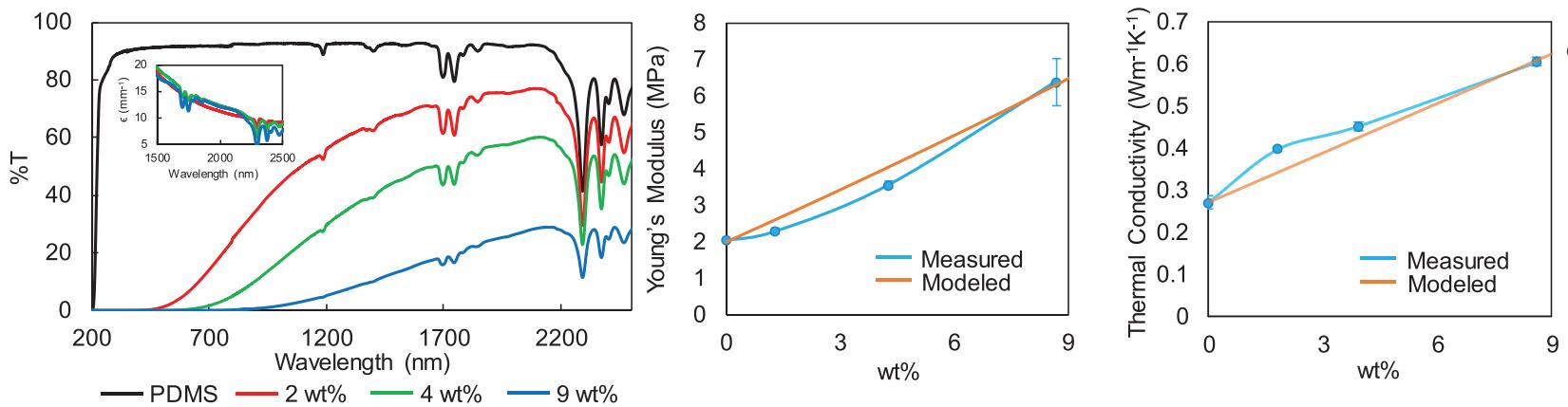
Piezoelectric Properties of BNNT/PDMS



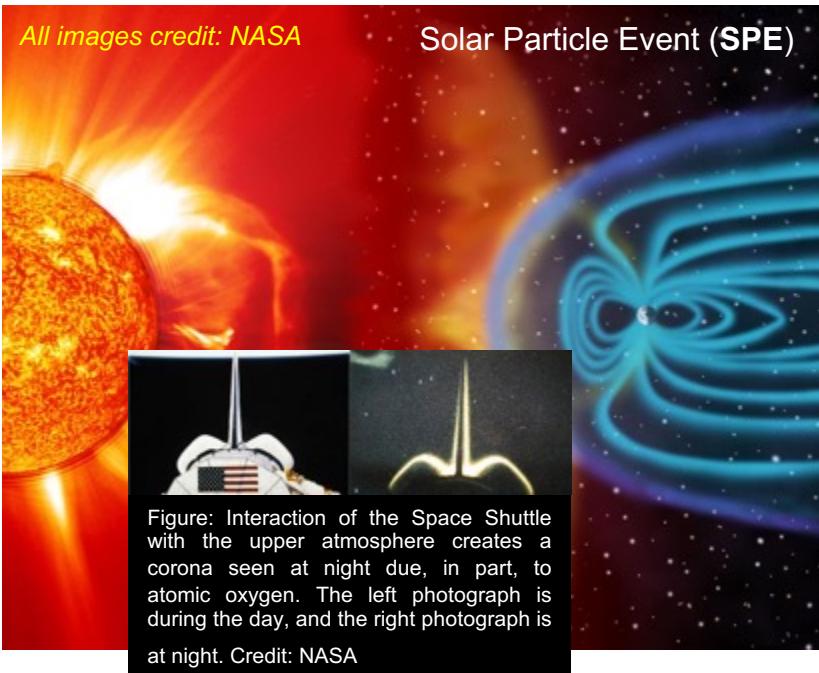
Alignment Effect & Vibration Sensing of BNNT/PDMS



Optical, Mechanical, and Thermal Properties of BNNT/PDMS



Radiation Shielding Properties

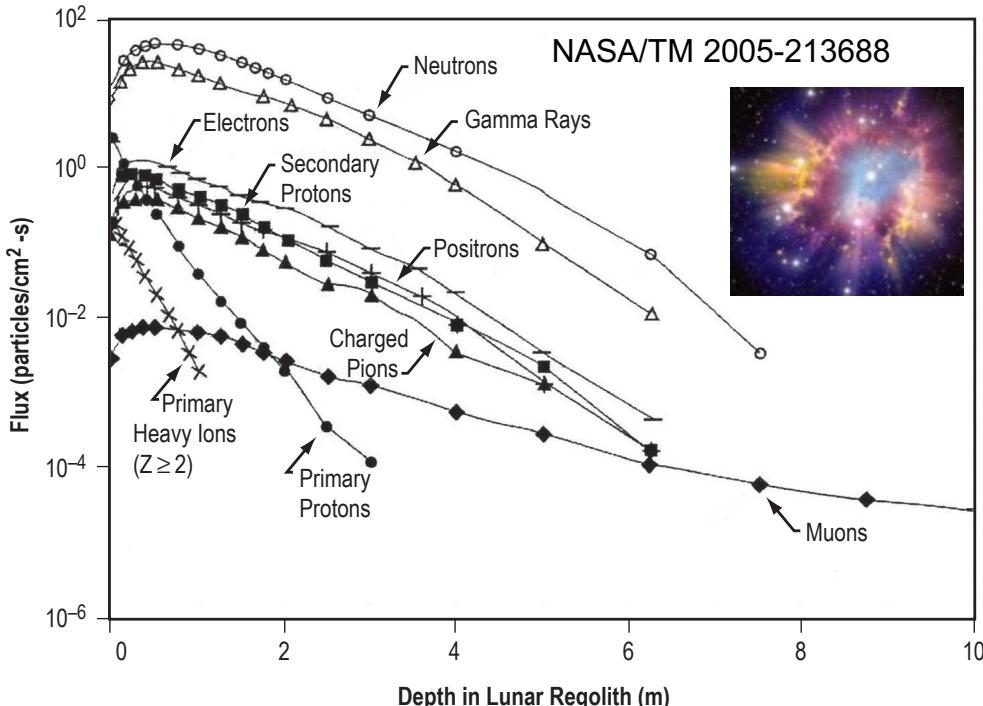


Measurements of Energetic Particle Radiation in Transit to Mars on the Mars Science Laboratory

C. Zeitlin,^{1,*} D. M. Hassler,¹ F. A. Cucinotta,² B. Ehresmann,¹ R. F. Wimmer-Schweingruber,³ D. E. Brinza,⁴ S. Kang,⁴ G. Weigle,⁵ S. Böttcher,³ E. Böhm,³ S. Burmeister,³ J. Guo,² J. Köhler,³ C. Martin,³ A. Posner,⁶ S. Rafkin,¹ G. Reitz⁷

The Mars Science Laboratory spacecraft, containing the Curiosity rover, was launched to Mars on 26 November 2011, and for most of the 253-day, 560-million-kilometer cruise to Mars, the Radiation Assessment Detector made detailed measurements of the energetic particle radiation environment inside the spacecraft. These data provide insights into the radiation hazards that would be associated with a human mission to Mars. We report measurements of the radiation dose, dose equivalent, and linear energy transfer spectra. The dose equivalent for even the shortest round-trip with current propulsion systems and comparable shielding is found to be 0.66 ± 0.12 sievert.

Galactic Cosmic Ray (GCR) and produced Secondaries in lunar regolith



Spacecraft data nails down radiation risk for humans going to Mars

Nature News, May 30, 2013, Ron Cowan

Interviewed Sheila Thibeault at NASA Langley about the study published in *Science*

Mars Science Laboratory (MSL) during its cruise to Mars between 6 December 2011 and 14 July 2012 (253 days)

Mars Round Trip Dose Equivalent is around 0.66 Sievert

MRS Bulletin 40 836 (2015)

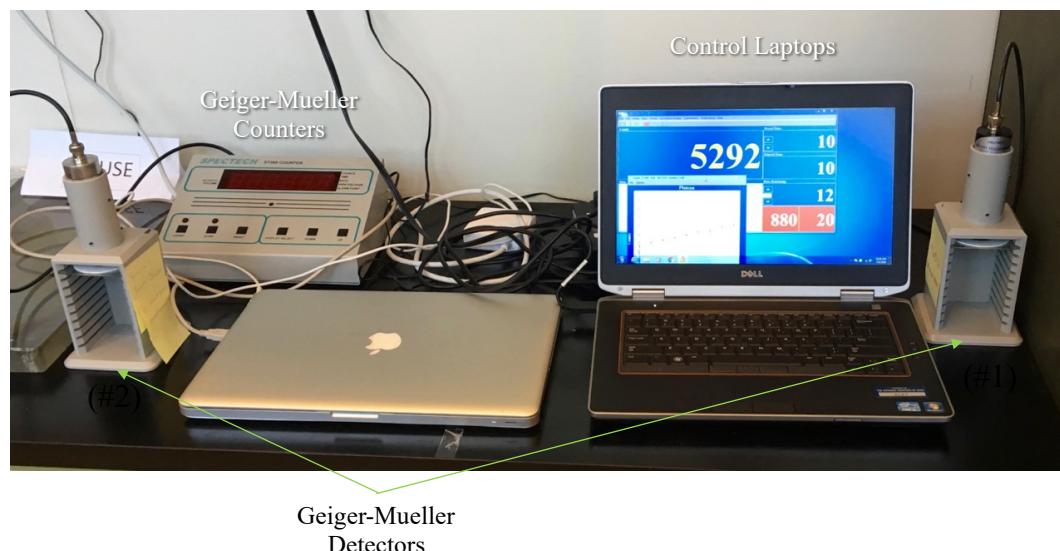
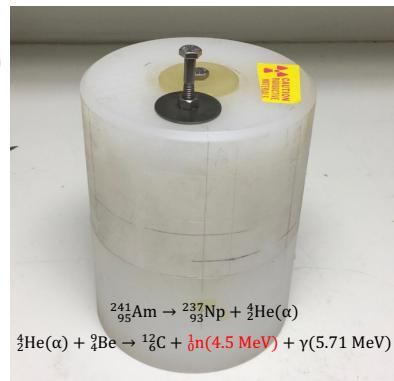
Radiation Tests: LaRC Radiation Exposure Test Facility

Neutron Source

- Radioactive Source: Am/Be (1 Curie) source produces fast neutron (4.5 MeV) and thermal neutrons (<0.5 eV) by borated PE cylinder (44 mm thick)
- Sample: 2"x 2"
- Detection Foil: 1.25" Indium Foil (0.5mm, 19 barns), $^{115}\text{In}(n, \gamma)^{116}\text{In}$

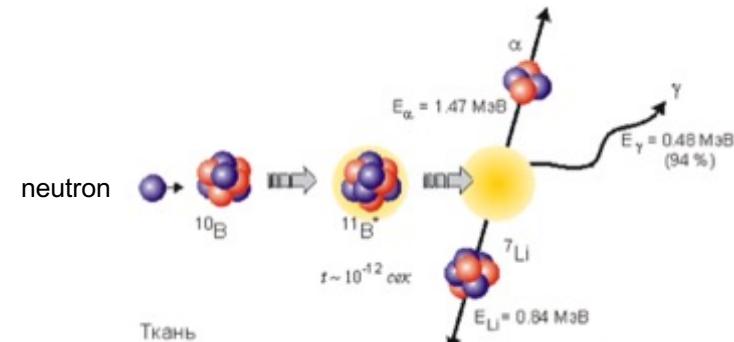
Low Dose Rate

(45 mrem/hr, dose equivalent rate)

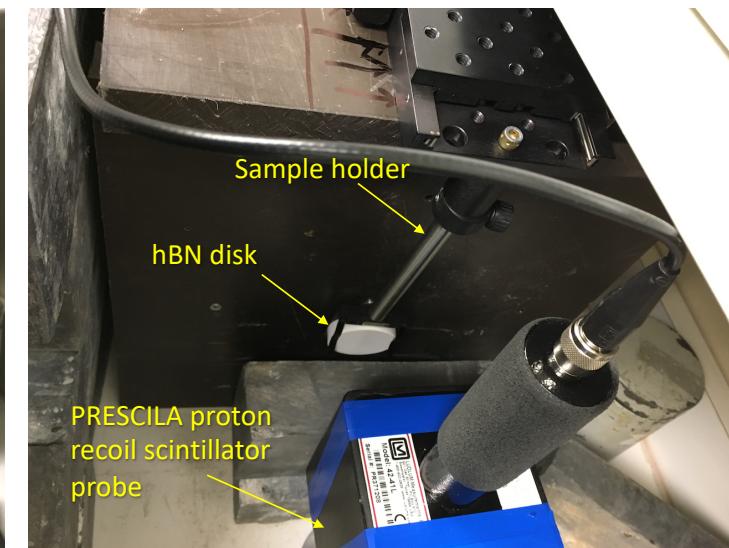
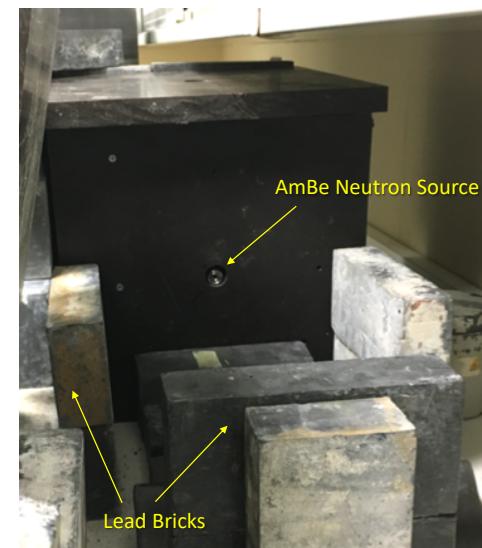


High Dose Rate

(800 mrem/hr, dose equivalent rate)



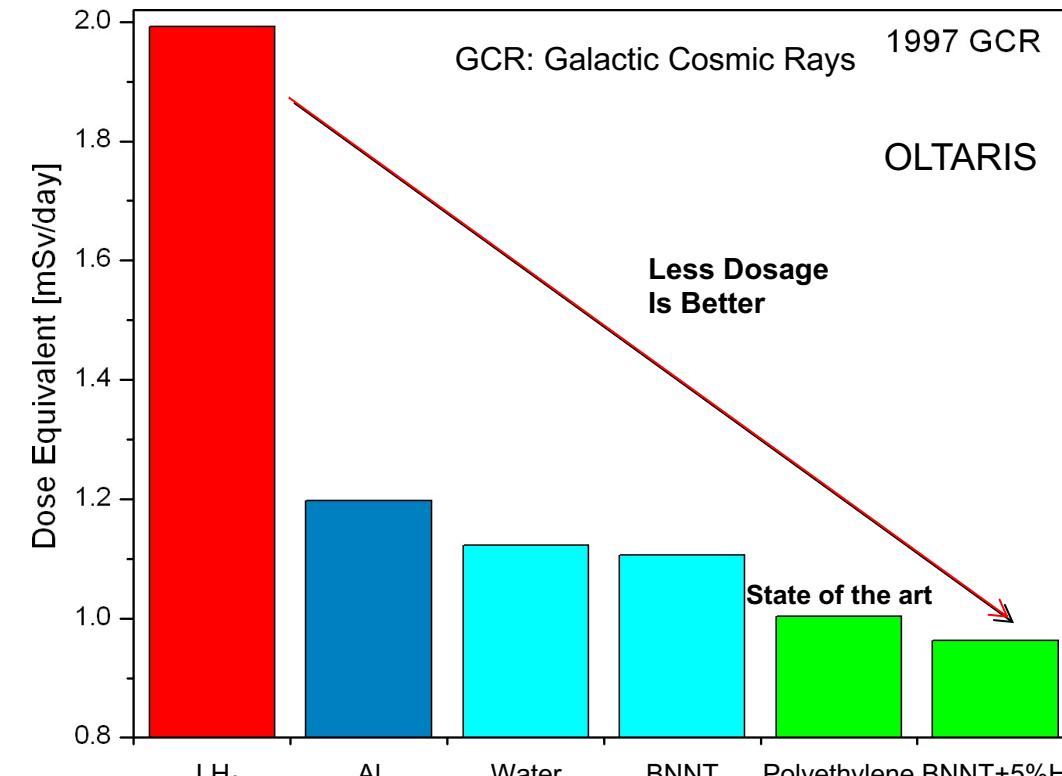
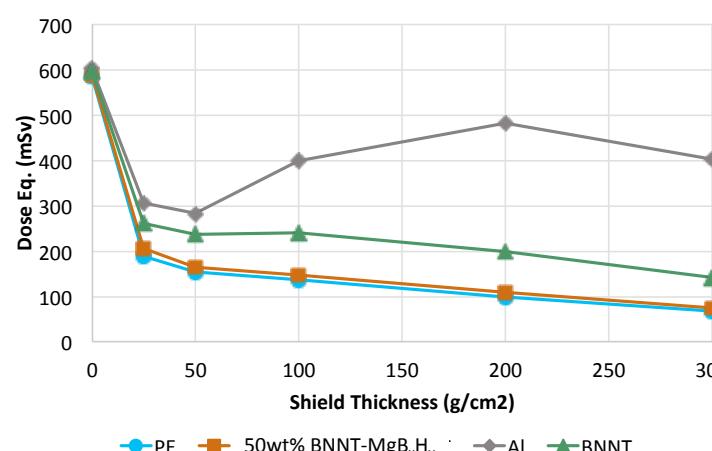
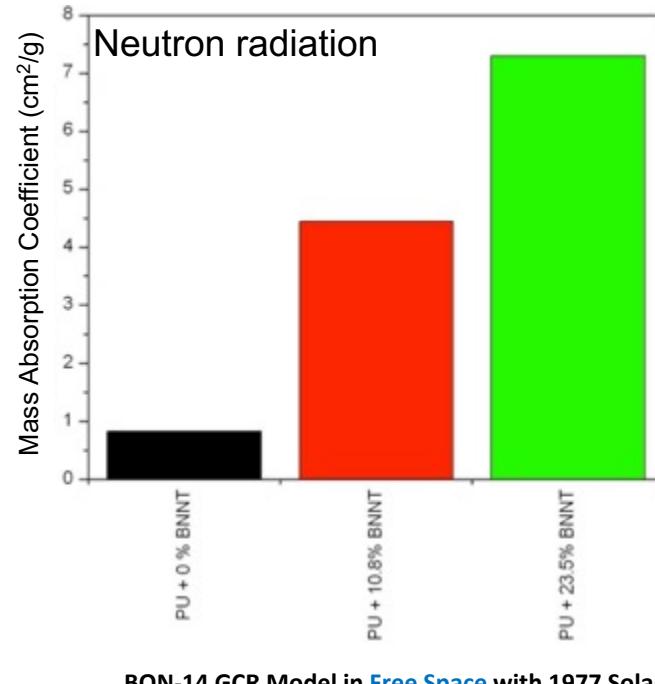
<http://www.inp.nsk.su/bnct/introduction/introduction.en.shtml>



Dose Equivalent Rate Measurement

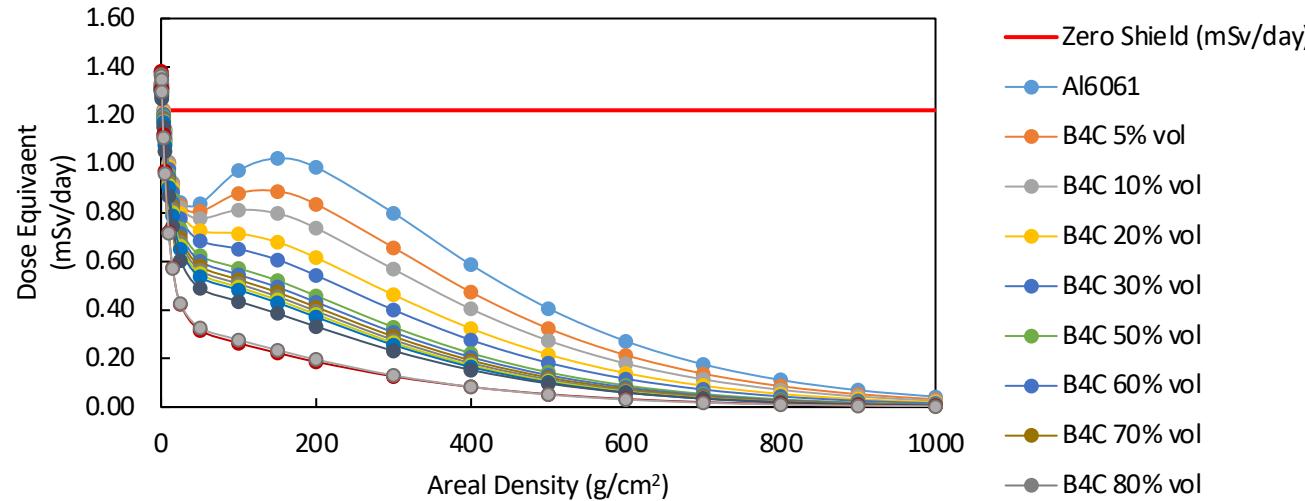
- Neutron survey meter: Ludlum Portable Survey, Model 2363
- Probe: PRESCILA proton recoil scintillator probe (Model 42-41L)
- Detection range: 0.1 mrem/hr to 1 rem/hr

Radiation Shielding Effectiveness of BNNT Composites

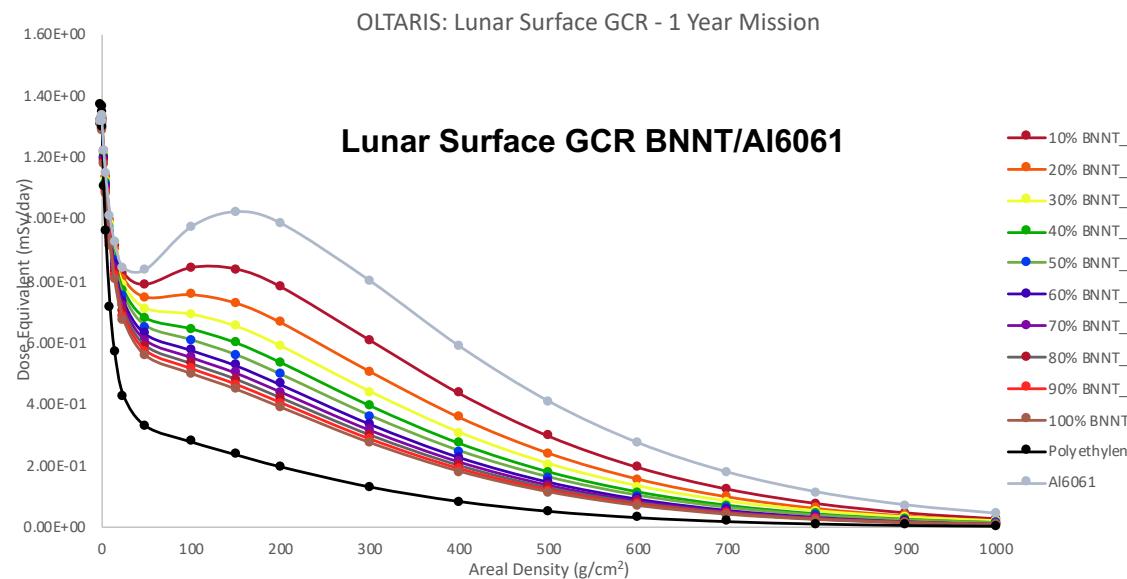


OLTARIS: GCR Lunar and Mars Surface Environment

BON-14 GCR Model on Lunar Surface with 1977 Solar Min. Incident on Vehicles with varying thickness: B₄C/AI6061

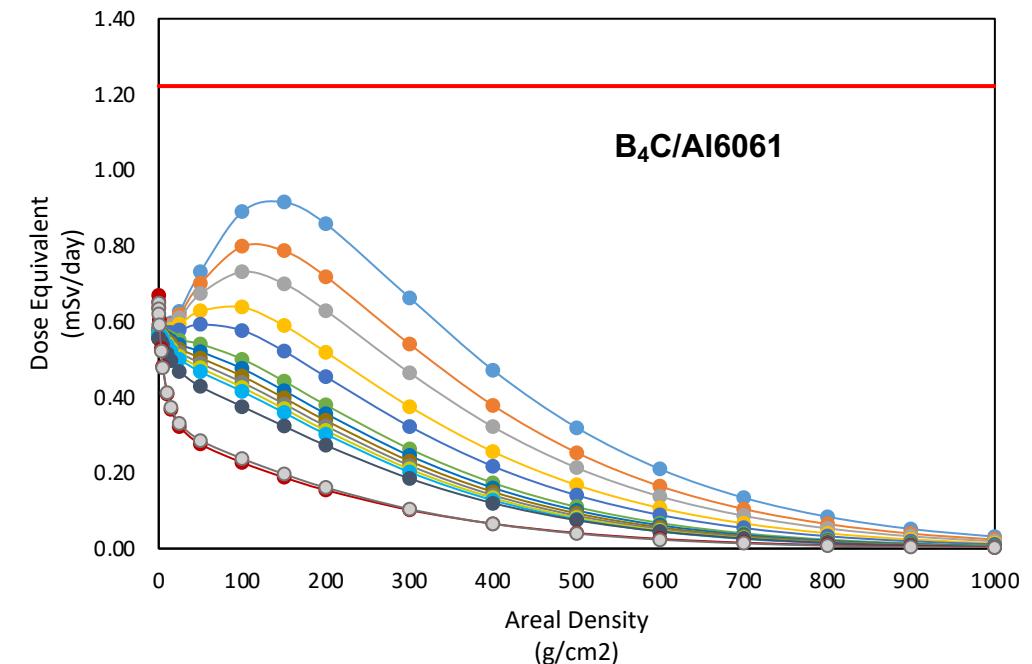


Parameters
 Environment Selection: GCR, Lunar Surface
 Mission Definition: Select historical Solar Min/Max
 Historical Min/Max: August 1972 (King)
 Mission Duration Days: 365



Parameters
 Environment Selection: GCR, Mars Surface
 Mission Definition: Select historical Solar Min/Max
 Historical Min/Max: August 1972 (King)
 Mission Duration Days: 365
 Mars Surface Parameters: MarsGRAM Atmosphere Elevation: 0.0 km

BON-14 GCR Model on Mars Surface with 1977 Solar Min. Incident on Vehicles with varying thickness



Summary



- High Temperature-Pressure BNNT synthesis method was introduced.
- BNNT dispersion was successfully achieved by thermodynamic approach using Hansen solubility parameters for single and co-solvent systems.
- Interfacial shear strength and fracture energy of BNNT with polymer, metal, and ceramic matrices were superior to those of CNT.
- BNNT exhibited excellent thermal stability under a simulated planetary entry environment along with flame resistance and retardation properties
- BNNT and BNNT polymer composites exhibited excellent piezoelectricity as well as electrostrictive behavior even without poling.
- BNNT exhibited excellent neutron radiation shielding effectiveness and hydrogen containing BNNT showed superb shielding effectiveness against GCR and SPE.

Acknowledgements

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Rice University

Mohammad Adnan, Daniel Marincel, Matteo Pasquali

Georgia Tech

Huibin Chang, Prabhakar Gulgulje, Jeffrey Luo, Satish Kumar



NASA C&I, B&P, GCD, IRAD, CIF, NIAC, ECI

NASA Education Programs

NASA Internship, Fellowship, and Scholarship (NIFS)

<https://intern.nasa.gov/>

NASA Space Grant

<https://www.nasa.gov/stem/spacegrant/about/index.html>

NASA Pathways Program

<https://www.nasa.gov/careers/pathways-program>

NASA Space Technology Graduate Research Opportunities (NSTGRO)

<https://www.nasa.gov/directorates/spacetech/strg/nstgro>

NASA Fellowship

<https://www.nasa.gov/stem/fellowships-scholarships/index.html>